STUDIES IN GEOPHYSICS

Groundwater Contamination

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Panel on
Groundwater Contamination

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Preface

This study is part of a series of studies in geophysics that have been undertaken for the Geophysics Research Forum by the Geophysics Study Committee. One purpose of each study is to provide assessments from the scientific community to aid policymakers in decisions on a societal problem that involve geophysics. An important part of such assessments is an evaluation of the adequacy of current geophysical knowledge and the appropriateness of current research programs as a source of information required for those decisions.

This study on groundwater contamination was initiated by the Geophysics Study Committee and the Geophysics Research Forum with consultation of the liaison representatives of the agencies that support the Geophysics Study Committee, relevant committees and boards within the National Research Council, and members of the scientific community.

The study addresses our current scientific understanding of groundwater contaminant transport—both by theory and by investigation of contaminated aquifers. The study also looks at many of the fundamental questions and uncertainties that require additional scientific research for the prediction of contaminant transport and the control of groundwater contamination.

The preliminary scientific findings of the authored chapters were presented at an American Geophysical Union symposium in San Francisco in December 1981. In completing their chapters, the authors had the benefit of discussion at this symposium as well as the comments of several scientific referees. Ultimate responsibility for the individual chapters, however, rests with their authors.

The Overview of the study summarizes the highlights of the chapters and conclusions and recommendations. In preparing the Overview, the pan(
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of groundwater contamination. Chapter 1 briefly examines th(

of the problem. Chapters 2 and 3 review the scientific understanding of contaminant transport and chemistry. Chapters 4 and 5 review some of the problems associated with waste-disposal methods. Chapters 6 through 12 give specific examples of groundwater contamination, the nature of the scientific problems, and the scientific problems involved in waste disposal and aquifer reclamation. The final two chapters, 13 and 14, introduce some of the institutional considerations for waste disposal and the prevention of groundwater contamination.

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THE PROBLEM

The reliable assessment of hazards or risks arising from groundwater contamination problems and the design of efficient and effective techniques to mitigate them require the capability to predict the behavior of chemical contaminants in flowing groundwater. *Reliable and quantitative predictions of contaminant movement can be made only if we understand the processes controlling transport, hydrodynamic dispersion, and chemical, physical, and biological reactions that affect soluble concentrations in the ground.* This report addresses the status of scientific understanding of transport of contaminants in groundwater in terms of hydrologic theory (Chapters 2 and 3) and case studies of occurrences of groundwater contamination (Chapters 6-12).

The widespread use of chemical products, coupled with the disposal of large volumes of waste materials, poses the potential for widely distributed groundwater contamination. New instances of groundwater contamination are continually being recognized. Hazardous chemicals, e.g., pesticides, herbicides, and solvents, are used ubiquitously in everyday life. These and a host of other chemicals are in widespread use in urban, industrial, and agricultural settings. Whether intentionally disposed of, accidentally spilled, or applied to the ground for agricultural reasons, some of these chemicals can eventually reach the groundwater and contaminate it. Because of the volumes of toxic wastes and because of their stability in groundwater, such contamination can pose a serious threat to public health.

Groundwater is the subsurface transporting agent for dissolved chemicals including contaminants. Materials dissolved from the wastes may be transported from the burial or disposal site by groundwater flow, with the result that the quality of water from wells is reduced by the contaminated groundwater. In addition, natural discharges of an aquifer, such as at springs and seeps, can return a contaminant to the surface. Because of the slow rates of groundwater movement and natural flushing of aquifers, when areas are contaminated, they commonly remain so for decades or longer. The major geophysical inputs to the problems of waste disposal and groundwater contamination deal with the chemistry and rates and directions of contaminant transport.

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The challenges are (1) to prevent the introduction of contaminants in an aquifer, (2) to predict their movement if they are introduced, and (3) to remove them, to the extent possible, to protect the biosphere effectively.

The largest potential source of contamination of groundwater is the disposal of solid and liquid wastes. During the past several decades, legislation reflecting environmental concerns has attempted to restrict air and surface-water pollution; this has resulted in increased disposal of wastes in the subsurface. In 1980, the U.S. Environmental Protection Agency (EPA) estimated that there were 200,000 landfills and dumps receiving 150 million tons per year of municipal solid wastes and 240 million tons per year of industrial solid wastes. In addition to landfills, 176,000 surface impoundments receive 10 trillion gallons per year of liquid industrial wastes. The results of the EPA surface impoundment assessment are shown in Table 1.

Not all wastes are hazardous. However, the EPA (1980) estimated that 142,000 tons of hazardous wastes are generated daily in the United States—approximately 60 million tons annually. These wastes are generated at more than 750,000 sites. To some extent many of the larger industrial sites had, in the past, landfills on their property, which received much of their plants' waste. The EPA (1980) estimated that 50,000 such sites have been used, at some time, for the disposal of hazardous wastes. Of these, 1200 to 2000 are thought to pose threats to the environment.

Waste disposal is not the only source of groundwater contamination. As additional sources, the EPA (1980) also lists septic systems, agriculture, accidental leaks and spills, mining, highway de-icing, artificial recharge, underground injection, and saltwater encroachment.

Current estimates of the extent of groundwater contamination suggest that 0.5 to 2.0 percent of the groundwater in the conterminous United States may be contaminated (see Chapter 1). Although this might not seem to indicate a large problem, *much of the contamination occurs in areas of heaviest reliance on groundwater.*

Several ground-burial disposal practices and repositories have been in use for many years and have been shown to cause minimal or no groundwater contamination. However, some waste-disposal practices have resulted in irreversible contamination of groundwater. The examples of Love Canal, the EPA list of more than 400 contaminated sites, and others indicate the magnitude of the resulting groundwater contamination problems with possible health hazards and other deleterious effects.

Restoration of contaminated aquifers can be extremely expensive. This may involve

TABLE 1 Preliminary Findings of the EPA Surface Impoundment Assessment[a]

Category	Sites Located	Impoundments Located	Sites Assessed
Industrial	10,819	25,749	8,193
Municipal	19,116	36,179	10,675
Agricultural	14,677	19,167	6,597
Mining	7,100	24,451	1,448
Oil/gas brine pits	24,527	64,951	3,304
Other	1,500	5,745	327
Totals	77,739	176,242	30,544

[a]The Surface Impoundment Assessment also released analysis based on data from the assessed industrial sites.
• Almost 70 percent of the industrial impoundments are unlined.
• Only 5 percent are known to be monitored for groundwater quality.
• About one third of the impoundments contain liquid wastes with potentially hazardous constituents.
• Analysis of sites for the chemical and allied products industry reveals similar findings with the exception that over 60 percent of the sites may contain liquid wastes with potentially hazardous constituents.

drilling many wells and pumping vast quantities of groundwater. The pumped water can often be treated, to reduce the concentration of contaminants, and reinjected into the aquifer. For example, the current estimated costs for contaminant *containment* efforts at the Rocky Mountain Arsenal, Colorado, are about $100 million; the cost estimates for "total" *decontamination* of the Arsenal range from $800 million to $1 billion (U.S. Army, 1982). The question of cost/benefit trade-offs to society in these cases needs to be examined carefully; some sites may prove to be so expensive to restore that they may have to be designated as permanently contaminated.

The subsurface can be used for waste repositories. However, such repositories should be selected, designed, and engineered in terms of the hydrology, geology, hydrogeo-chemistry, and microbiology of a particular site and the characteristics of the specific wastes. Care must be taken to provide isolation of potentially toxic substances from the biosphere for long periods of time. The necessary isolation time depends on the toxicity of the particular contaminant and on the extent to which the substances will be degraded or diluted to below toxic levels over time with a high degree of certainty. For example, current estimates concerning high-level radioactive wastes suggest that a period of isolation from the biosphere of 1000 to 10,000 years will allow decay of many of the hazardous radionuclides to safe levels (NRC, 1983). However, certain nondegradable highly toxic substances along with some of the radioactive wastes with very long-lived radionuclides may require permanent isolation.

If the subsurface is to be utilized as a repository of wastes, both increased scientific knowledge and improved engineering techniques must be brought to bear on the problem of groundwater contamination. The development of better methods for managing and disposing of today's waste and for rectifying yesterday's mistakes will be necessary. The scientific problem is one of understanding the physical-chemical-biological system sufficiently well to be able to predict the movement and fate of contaminants. This challenge is not met easily, but with concentrated effort it should be possible to isolate toxic substances in the ground in certain types of environments in a way that will pose no hazards.

There seems to be a general, although inaccurate, impression that little is known about the occurrence of groundwater and that the science of groundwater hydrology is in its infancy. This stems in part from the fact that groundwater occurs in the subsurface, out of sight, and can only generally be investigated indirectly, e.g., through observations made in boreholes.

Problems of flow through porous media have been investigated since the work of Henry Darcy in 1856. Flow and transport in the subsurface continue to be studied in petroleum engineering, groundwater hydrology, soil science, and, to some extent, chemical engineering. While the applications of the scientific knowledge often differ, the physical and chemical processes that apply are the same. These disciplines complement one another, and to a large extent technology has been exchanged between them.

During the course of this study, it became apparent that the unsolved technical problems dealing with groundwater contamination pale beside the institutional issues (introduced in Chapters 13 and 14) and the public's perception of risk associated with waste disposal. Past economic considerations may be interrelated with the problems associated with groundwater contamination. The disposal of wastes in the ground has often been viewed as attractive because of the slow movement of groundwater relative to the rapid contaminant transport in surface waters or the atmosphere. Therefore, the potential cleanup costs were delayed—costs that did not constitute part of the then current operational expenses. In addition, costs that might be incurred decades later took account of the present and future value of the dollar. This leads to the question: Is the present worth of such far-off future costs truly so small or negligible that it makes no "economic" sense to invest now to prevent those future damages? Although we do

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not have an answer to this question, we should consider that the physical reasons responsible for slow groundwater transport are the same reasons that make the cleanup and mitigation of its contamination more difficult and expensive.

Because hazardous chemicals are so widely used, their disposal in a safe and effective manner is especially difficult. The Resource Conservation and Recovery Act (RCRA) legislated a "cradle to grave" manifest control system for hazardous substances. The system is intended to track the whereabouts of hazardous materials until they are used or disposed of. In most past practice, the records kept on the nature and volume of wastes disposed of in a particular site have been incomplete. This has created one of the problems in analyzing the movement of contaminants in that the source of pollutants is usually poorly known. Until the system legislated by the RCRA is effectively implemented, the whereabouts of hazardous materials will remain uncertain.

Environmental legislation—the Safe Drinking Water Act, the Resource Conservation and Recovery Act, and the Comprehensive Environmental Response Compensation and Liability Act (commonly referred to as Superfund)—further restrict disposal of wastes in or on the solid earth. Taken collectively, the environmental legislation, which has restricted the use of the air and surface water for disposal of wastes, has now limited the use of the land for waste disposal. Clearly a modern society must either dispose of the enormous quantities of residual products (wastes) that it generates or in some way reprocess those residuals. While restrictions placed by legislation protect the environment, *one can question whether we have moved very far toward developing a rational strategy of waste disposal that provides long-term protection to society and the environment.* A strategy of disposal or reprocessing, or both, must be forthcoming if we are to act responsibly toward future generations.

GROUNDWATER: THE RESOURCE

Groundwater is a heavily used resource; its magnitude has been described in the *U.S. Water Resources Council Bulletin 16* (1980):

The Nation's groundwater resource is enormous—it is our largest freshwater source in terms of volume in storage. Beneath the conterminous United States lie some 65 quadrillion gallons or 200 billion acre-feet of groundwater within a few thousand feet of the land surface, part of which is replenishable upon use. However, it should be recognized that not all of this water is practicably recoverable. Withdrawals amounted to about 83 billion gallons a day in 1975. This withdrawal is approximately 20 percent of the total withdrawal use of water in the Nation excluding hydroelectric use; it constitutes only a fraction of the groundwater development possible.

Groundwater constitutes a significant source of water in almost all of the United States, particularly in the West, where it is heavily used for irrigation. California alone accounts for 23 percent of national groundwater use, and California and Texas together account for 37 percent.

SOURCES OF GROUNDWATER CONTAMINATION

Almost every major industrial and agricultural site has in the past disposed of its wastes on site, often in an inconspicuous location on the property. Every municipality has had to dispose of its waste at selected locations within its proximity. Accidental spills of toxic chemicals have also occurred, often without particular attention to or concern for the consequences—some practices of cleaning a toxic spill involve flushing it with water until it disappears into the ground. Past waste-disposal practices and dealing with spills have not always considered the potential for groundwater contamination.
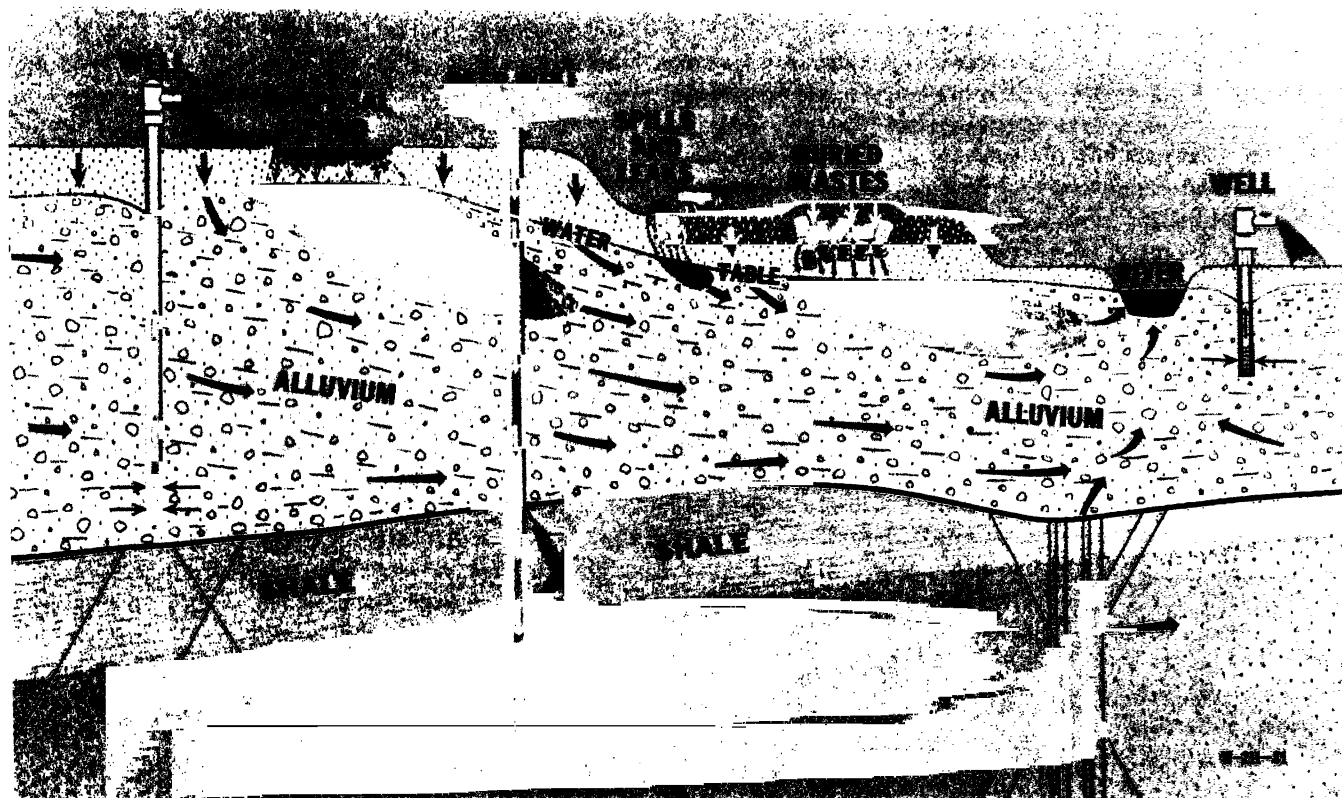
FIGURE 1   Schematic representation of contaminant plumes possibly associated with various types of waste disposal.

Groundwater contamination (see Figure 1) may be localized or spread over a large area, depending on the nature and source of the pollutant and on the nature of the groundwater system. A problem of growing concern is the cumulative impact of contamination of a regional aquifer from nonpoint sources (i.e., those that lack a well-defined single point of origin), such as those created by intensive use of fertilizers, herbicides, and pesticides. In addition, small point sources—such as numerous domestic septic tanks or small accidental spills from both agricultural and industrial sources—threaten the quality of regional aquifers. The situation on Long Island, New York, illustrates the impact of widely distributed small point sources of pollution on an aquifer system where approximately 3 million residents rely on wells as their sole source of water supply. Domestic wastewater seeping from thousands of septic systems and leachates from landfills and industrial waste-disposal sites have contaminated the shallow groundwater in many parts of Long Island, as described in Chapter 9. Research is needed to evaluate the groundwater resources threatened in this manner in order to understand how contamination from such diffuse sources is attenuated by dispersion and chemical reactions in the groundwater systems.

Septic tanks are a frequently used method for disposal of sewage. Where they are properly sited, such as in sparsely populated areas and in soils with good drainage above the water table, septic tanks generally pose little or no hazard. All too frequently, however, they are installed with drain fields that are too small and intersect nearby groundwater supply wells. In such situations, sewage often contaminates wells in the area or moves to the land surface, or both. Even where septic systems are well drained, they may eventually pollute the groundwater. The EPA (1980) found that about a third

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of all septic tank installations are not operating properly and that the consequent pollution both above and below ground is substantial. The solution to groundwater contamination from septic systems, beyond better engineered on-site facilities or improved maintenance, may lie in better land-use control and in effective regulations for septic tank installation.

Sewage-disposal activities are introducing viruses into a variety of groundwater sources; but the persistence and movement of these viruses has only recently become the subject of scientific inquiry, and the extent to which such viruses in groundwater pose a hazard to public health is still largely unknown.

Recent technological advances have made it possible to recover minerals that occur in low concentrations in the Earth's crust through in situ leaching. (Uranium is commercially mined by this method.) Research on methods of recovering disseminated copper has led to similar techniques being applied at several southwestern U.S. copper mines. By combining injection and production wells in a manner similar to their use in oil reservoirs, groundwater flow through the ore body is controlled. Chemical reagents are usually introduced that make the mineral of interest more soluble and thereby more economically recoverable by the moving fluids. In Texas, uranium is being mined by in situ leaching in rocks that have a potential for use as a freshwater supply. Care must be taken to flush out or neutralize the uranium-leaching solutions, which, if they remained, would contaminate the aquifer (see Chapter 12).

The removal of the injected chemical reagents following mining can be made more complicated if the reagents are dispersed in the groundwater. Dispersion requires circulation of larger quantities of fluid than originally envisaged to accomplish adequate cleanup. Only in a small number of mining operations has such cleanup been undertaken. None has completed the stage of groundwater restoration, although a few pilot operations are in progress.

DISPOSAL PRACTICES

A number of practices have resulted in migration of waste products to the subsurface (see Figure 1). Among these are the following: landfills and dumps, evaporation ponds or lagoons, septic systems (addressed earlier), coal and mineral tailings piles (see NRC, 1981a, 1981b), and deep burial and deep injection. Each of these disposal methodologies presents technical and hydrogeologic problems and the potential for groundwater contamination.

Landfills

Landfills are probably the most widely used means of solid-waste disposal. Several chapters in this report (Chapters 4, 7, 8, and 10) specifically discuss landfills and some of their associated groundwater problems. The problems are often related to the hydrogeologic setting of a specific landfill. In our efforts to restore contaminated aquifers, we need to consider this hydrogeologic setting carefully.

The potential for groundwater contamination from landfills was recognized several decades ago. One of the more common measures taken to avoid groundwater contamination is to locate landfills in areas composed of rock or soil of low permeability so that water does not percolate through the landfill into the underlying aquifer. However, recent studies of landfills situated in low-permeability rocks indicate that in humid areas many of the landfill trenches in which the wastes are buried become filled with water from rain and snow. This surface water seeps downward through the landfill cover, fills the trenches, and eventually overflows—the so-called "bathtub" effect. In these in-

stances the contamination is not a groundwater problem, which would result from water in the trenches seeping downward to underlying aquifers, but rather a surface-water problem. One approach taken to avoid the surface-water problem has been to cover the trenches with a low-permeability material. However, the wastes when placed in the landfill are often poorly compacted and decay with time; the wastes in the trench become naturally compacted and can result in breaching the cover, which allows the trench to become saturated, eventually overflowing the bathtub. This effect is difficult to overcome.

A possible solution to the bathtub effect is to design the landfill with a controlled leak. This requires draining the landfill from below—either naturally with an underlying aquifer or with installed drains. In the case of an underlying aquifer, the groundwater flow would need to be large enough to dilute the contaminants below toxic levels. Alternatively, the drainage from the landfill can be collected and processed through water-treatment plants. Careful hydrologic and engineering analyses are needed to design systems that will prevent the occurrence of unacceptable levels of both groundwater and surface-water contamination.

Evaporation Ponds and Lagoons

Evaporation ponds and lagoons are used widely for disposal of wastes dissolved in water. The technique allows the water to evaporate, leaving behind a concentrated solid residue, which can be disposed of more readily than the liquid wastes. However, such ponds and lagoons often leak and contaminate the underlying groundwater. Attempts to rectify the problem include lining the pond to reduce the leakage. But it is difficult to add an impermeable lining that will function for prolonged periods (usually a decade or longer). Few, if any, economically feasible materials currently available can resist corrosion from a broad range of chemicals and still maintain physical strength great enough to resist mechanical failure. A number of substances such as plastic linings and layers of low-permeability clays have been used with some success. As discussed in Chapter 6, evaporation ponds have been used extensively at the Rocky Mountain Arsenal for waste disposal. Initially these ponds were unlined and resulted in widespread contamination of the groundwater. However, even a lined pond at the Rocky Mountain Arsenal was found to have leaked after more than 20 years of use.

Deep Injection or Burial

Deep burial of toxic wastes has several advantages over shallow burial or surface-storage systems. The most important advantage is that contaminants that may become dissolved in groundwater will not migrate directly to the land surface. The increased length of the groundwater flow path allows time for decomposition of unstable chemical compounds, the decay of radionuclides, and the dilution of toxic materials by dispersion. Deep burial also affords protection against the possibility that hazardous materials will be exposed at the surface through slow processes of erosion. The depth of burial is generally related to rock permeability; the deeper the burial, the lower the permeability. On the basis of hydrogeologic criteria alone, many different rock types would seemingly provide safe repositories at depths greater than 100 m.

Deep repositories in most locations will eventually fill with water. However, if zones of significant groundwater circulation are avoided, repositories at depths of more than 300 m in granitic rocks would be likely to take several hundred years to fill with water once they are closed. In a well-placed repository, several thousand years may be needed for a simple piston-flow displacement of all the water in the flooded repository (see Chapter 5).

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Although deep injection or burial is a suitable method for the disposal of toxic wastes, a number of site-specific scientific and engineering problems need to be considered. For example, a method proposed for the disposal of high-level radioactive wastes is a deep repository (approximate 1 km) in crystalline rocks (see NRC, 1983). Unfortunately, most crystalline rock masses are fractured to some extent. This poses problems for hydrologists because flow and transport in fractured rocks are not well understood. While this is an area of active research, currently there is no consensus within the hydrogeologic community on the theory of how to treat flow and transport in fractured rocks. As a result, predictions of groundwater flow and transport for several thousand years in fractured rocks are difficult to provide with a high degree of confidence.

Each borehole or shaft to a repository or disposal horizon represents a short circuit along which wastes could flow back to shallow levels and interact with the biosphere. The engineering problems in effectively plugging such holes with seals that will isolate the repository for periods of several thousand years are not simple.

While deep disposal is undoubtedly one of the preferred methods of waste disposal for highly toxic wastes, its most serious disadvantage is its cost. Deep repositories will be expensive to construct and difficult to monitor; and if errors are made or unexpected flaws are uncovered, they will be costly to correct (e.g., removing the waste and placing it in a better location or a better designed repository).

Multiple Barriers

For deep repositories the approach currently favored from the vantage point of risk analysis by both the military and the U.S. Department of Energy involves the concept of multiple barriers. A number of engineered barriers would include: (1) waste forms that are not readily soluble, (2) canisters that would isolate the wastes for long periods, and (3) backfilling the repositories with materials that are highly sorptive and of low permeability. The engineered barriers may then be coupled with a number of natural barriers including: (1) storage in low-permeability media; (2) siting in areas where the natural groundwater flow moves contaminants away from the biosphere, at least in the immediate vicinity of the repository, if not regionally; and (3) siting in rocks containing naturally occurring minerals (e.g., zeolites) that tend to sorb the contaminants or in highly porous rocks (e.g., tuffs) in which diffusion into the matrix can be a retardant during fracture flow. At Oak Ridge National Laboratory, in a use of the concept of multiple barriers, radioactive wastes have been mixed with cement and implaced by hydraulic fracturing techniques in low-permeability shale.

In the arid and semiarid portions of the western United States, thick unsaturated zones often overlie a deep water table. Studies of waste disposal, especially in the more arid areas of Nevada, suggest that there is limited or no transport of wastes through the ground in this environment. The natural movement of moisture through the unsaturated zone appears, at least from preliminary scattered observations, to be too small to transport significant amounts of wastes.

Numerous closed hydrologic basins exist within Nevada, Utah, and parts of adjacent states. These basins have thick unsaturated zones—in some places up to 600 m thick—and internal drainage, i.e., there is no discharge to the sea. Such closed basins in arid areas have an obvious advantage for waste-disposal purposes; even if the contaminants move, they will remain within the basin.

For long-term containment of wastes, climatic changes, such as were associated with the advances of Pleistocene ice sheets, should be considered in the prediction of waste movement. Sufficient work has been done at the Nevada Test Site to indicate that the water table did not change significantly during the more recent Pleistocene ice advances. The finding suggests that areas may be found where possible changes in climate will not significantly affect the rates of groundwater transport. Furthermore, the sorptive

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properties of most alluvium constitute a natural barrier to contaminant migration even if significant changes in groundwater flow were to occur (see Chapter 11).

EFFECTIVE DISPOSAL SITES

To some extent our past practice of waste disposal can be characterized as a strategy of "out of sight, out of mind." A number of disposal sites have proven to be effective in containment and reasonably safe. In some instances, careful thought and planning in site selection and disposal practices have led to safe containment of highly toxic wastes. However, siting must be done on a case-by-case basis (see, e.g., Chapter 4) and must depend on the nature of the wastes.

Unfortunately for scientific purposes, not many potential groundwater contamination problems have a history of investigation and a data base to document the situation. Some of the best-studied examples of field sites with the potential for groundwater contamination involve major nuclear test facilities. Investigations at some of these sites date back to the early 1950s, when studies were initiated by the Atomic Energy Commission. Geologists and hydrologists were consulted to help understand and monitor the potential migration of nuclear wastes. At several of these facilities, wastes have been implaced within the ground with a minimum of problems.

For example, most radionuclides from an underground nuclear explosion at the Nevada Test Site have experienced little or no migration in the groundwater from the region of release. This is because the Nevada Test Site, which is located in the Basin and Range province in an area of internal drainage, has appropriate geologic and hydrologic features and little precipitation, factors that minimize the migration of the radionuclides. The rocks, primarily volcanic tuffs and derived tuffaceous alluvium, contain large quantities of zeolites, which act as a natural exchange medium and tend to adsorb many of the contaminants, as suggested in Chapter 11. The high connected porosity of the tuffs further retards migration by diffusive processes. This characteristic is of particular importance in retarding the migration of nonsorbing species through fracture flow. In addition, if wastes were to enter the natural groundwater flow system, they would be transported over long horizontal distances for long periods of time, which would allow for radioactive decay of many of the more toxic radionuclides before they could be transported back to the near surface and the biosphere.

Another example of a site with appropriate hydrogeologic features resulting in effective containment is the Idaho National Engineering Laboratory (INEL, formerly the U.S. National Reactor Test Station, NRTS), which also involves the disposal of radioactive wastes. At INEL various wastes, including tritium (^{3}H), strontium-90 (^{90}Sr), and cesium-137 (^{137}Cs), have been discharged into the underlying Snake River Basalt Aquifer. Tritium has been transported conservatively (i.e., without chemical reactions other than radioactive decay); the dispersion is such that tritium concentrations are below hazardous levels once the contaminants have been transported several kilometers downgradient from the point of injection. Both ^{90}Sr and ^{137}Cs are adsorbed and remain tied to the aquifer skeleton within approximately 2 km of the injection well. None of the wastes poses significant hazards except in the immediate vicinity of the disposal site.

Other such suitable disposal sites can be found in a variety of environments through careful and innovative exploration and research. However, the necessary site-specific geologic and hydrologic data are frequently inadequate for a reliable evaluation to be made. As the Nevada Test Site illustrates, the subsurface can provide a natural migration barrier. If done with care, toxic wastes can be isolated from the biosphere for periods so long that they can be measured in terms of geologic time. The criteria are relatively simple: the total waste system—containers and repository as well as *geologic, geochemical*, and *hydrologic* setting—should isolate the wastes from the biosphere for a

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very long period. In consideration of organic wastes, additional criteria, such as *organic reactions* in and the *microbiology* of groundwater, need to be considered in the whole system.

GROUNDWATER HYDROLOGY

Conservative Transport

Effective utilization of the subsurface as a repository for wastes depends on information as to how the wastes are transported. Groundwater is the transporting agent, and it is generally agreed that we know a great deal about the flow of liquids through porous media. (In this case we define a porous medium as a typical aquifer or reservoir material—sand, gravel, sandstone.) However, the problem of contaminant transport is somewhat more complex than the problem of flow.

With conservative contaminant transport (transport without chemical reactions) a physical mixing occurs that is generally referred to as hydrodynamic dispersion. Dispersion is caused by both microscopic and macroscopic variations in the fluid velocity. The magnitude of dispersion is much larger under natural conditions in the field than in the laboratory— commonly 1000 to 10,000 times larger. The larger dispersion observed in the field is caused by the large-scale variations in fluid velocity produced by geologic deposits that commonly have a continuous spectrum of microscale to large regional-scale variations in permeability (the permeability of natural materials varies over 15 orders of magnitude). The matter of how best to characterize hydrodynamic dispersion is currently the subject of scientific debate; the status of our knowledge of the physical process is reviewed in Chapter 2.

As either tracers or contaminants are transported away from a source, the magnitude of the dispersion increases. This is reasonable because the large-scale mixing depends on the heterogeneity characterizing the geology of the site. As the contaminant moves it becomes more affected by the geologic heterogeneity, resulting in increased dispersion. Thus it becomes difficult to determine the dispersivity, the parameter most widely utilized to characterize dispersion, and tracer tests tend to become impractical. However, a number of field sites where contaminants have moved have now been studied. Investigations suggest that the dispersivity generally ranges from 10 to 100 m (the larger the dispersivity, the larger the dispersive mixing) once the contaminants have migrated several hundred meters or more.

Perhaps the most difficult and as yet unsolved problems in groundwater flow and transport are associated with fractured rock. Most crystalline rocks have been found to be fractured to great depth. Recent interest in utilizing crystalline rocks for waste repositories, particularly nuclear repositories, has focused on flow and transport through this type of rock.

Two schools of thought on the flow in fractured rock have evolved. One treats the flow in individual fractures and then aggregates these to form a flow system. The second deals with the fractured rock mass statistically. The difficulties in describing individual fractures, especially in the subsurface, have tended to persuade a growing number of investigators to treat the large-scale flow and transport problem in a statistical fashion. To understand and make reliable predictions of contaminant movement, it is necessary to know more about the relationships among primary geologic features, such as how porosity and permeability are related to geologic environments of deposition and how the number of fractures and their orientation and spacing are related to tectonic stresses. Not enough is known to allow quantitative predictions of the occurrence and nature of fractures in rocks.

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Transport with Reactions

Both inorganic and organic chemical reactions may occur during the transport process. The analyses of the problem of the reactions and their effect on transport are currently approached from two different directions: (1) studies of overall chemical equilibria and (2) transport analyses involving kinetics (in effect an irreversible thermodynamic approach), as pointed out in Chapter 3.

In the equilibrium approach one assumes that the reactions are sufficiently fast that chemical equilibrium generally is quickly achieved. In this approach the details of the transport process are not taken into account specifically. One need only apply the constraints of classical equilibrium geochemistry to understand the chemistry of the system. Knowing what chemical reactions to consider is not a trivial problem; it is of paramount importance. Much of the current work on chemical contamination has been approached from the framework of equilibrium geochemistry.

The transport approach relaxes the equilibrium assumptions. On the other hand, the mathematics is much more complex, and one must have some understanding of the kinetics of the reactions of concern.

The geochemistry of inorganic chemical constituents is better understood than that of organic constituents. Fortunately, under many conditions existing in nature, many of the inorganic contaminants are not particularly mobile. In the words of one member of the panel: "Mother Nature has been generally kind to us by impeding the transport of inorganic contaminants."

ORGANIC COMPOUNDS

Organic contaminants in groundwater are a major problem. The use of synthetic organic chemicals has grown at a phenomenal rate during this century; the growth has been especially rapid since World War II. A variety of organic compounds has gained widespread use in industry; agricultural pesticides and herbicides have been utilized extensively in recent years. For many of the organic compounds now in use, little is known about their toxicity. Some are believed to be hazardous at very low concentrations— tens or hundreds of parts per billion. In the past groundwater was not routinely tested for low levels of organic compounds; however, with the recognition that low-level organic contamination is a potential health hazard and with advances in the technology of analytical chemistry, increased instances of organic contamination have been identified. The chemical processes involved with organic contaminant transport are reviewed in detail in Chapter 3. As examples, Chapter 6, dealing with problems at the Rocky Mountain Arsenal, and Chapter 10, dealing with a landfill in Delaware, highlight some of the problems with organic contaminants.

Organic solvents, which are volatile in the atmosphere, move into unsaturated soils, often as a result of spills, and remain there for long periods—commonly tens of years. In an unsaturated soil, equilibrium is established between the liquid and the vapor phases of the contaminants. Each succeeding rain upsets the equilibrium and in the process carries some of the contaminant to the water table. Often the organic solvent remains as a source of groundwater contamination for long periods. Because some of these solvents are toxic at the parts per billion level, they pose particularly hazardous problems.

Recent research has established that many, if not most, of the chemical reactions involving organic compounds, in both the saturated and unsaturated zones, are controlled by microorganisms. Contrary to earlier studies, recent investigations have established high levels of microorganisms both above and below the water table; Wilson and McNabb (1983) summarized several sets of recent data, which are given in Table

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2. The amount of biomass identified is much larger that that which normally occurs in rivers and streams. The organisms identified are almost exclusively some form of bacteria.

The relationship between the concentration of the pollutant and its susceptibility for biotransformation is complex. Wilson and McNabb (1983) stated:

> . . . compounds that usually are considered degradable may not be transformed by the subsurface microorganisms if the compound is present at low concentrations. Similarly, compounds present at high concentration may only be partially degraded when oxygen is entirely depleted and can only be degraded further after dispersion or other physical processes mix the contaminated water with oxygenated water.
>
> [Table 3, this volume] presents the authors' opinions concerning the prospects for biotransformation of several important classes of organic pollutants in groundwater. These predictions are based on a cautious extrapolation from the behavior of these compounds in other natural systems and on our admittedly limited experience with their behavior in the subsurface. . . .

The control exerted by microorganisms on the chemistry of various organic contaminants is a particularly important area for increased future research. We have only begun to appreciate fully the importance of bacteria in controlling the chemical changes taking place. Only a limited number of situations and organic compounds has been investigated. With further study, it may be possible to control the degradation of particular contaminants in groundwater through the in situ introduction of certain cultures of microorganisms.

Many of the organic residuals are sufficiently stable in nature to remain intact indefinitely during groundwater transport. Future methods of coping with organic residuals may involve incinerating them at sufficiently high temperatures in order to break them down chemically. (Some toxic organics may not be totally broken down to nontoxic components using current incineration practices.) It may well be that the toxic organic compounds that cannot be incinerated or treated to make them less hazardous on a practical basis will have to be disposed of by deep burial, a method now proposed for radioactive wastes.

MATHEMATICAL ANALYSIS

One method of studying the transport of contaminants in groundwater is by mathematically simulating a field situation in which a well-defined contaminant plume has moved through time. This requires a historical set of data that defines the plume and documents the movement through time. Only a limited number of field sites exists

TABLE 2 Number (millions per gram of dry material) of Organisms in the Subsurface Environment[a]

Site	Depth to Water Table (m)	Subsoil	Just above Water Table	Just below Water Table
Lula, Okla.	3.6	—	—	—
February 1981	—	6.8	3.4	6.8
June 1981	—	9.8	3.7	3.4
Fort Polk, La.				
Borehole 6B	6.0	3.4	1.3	3.0
Borehole 7	5.0	7.0	1.3	9.8
Conroe, Tex.	6.0	0.5	0.3	0.6
Long Island, N.Y.	6.0	—	—	36
	3.0	170	—	—
Pickett, Okla.	5.0	—	—	5.2

[a]From Wilson and McNabb (1983) with permission of the American Geophysical Union.

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TABLE 3 Prospect of Biotransformation of Selected Organic Pollutants in Water-Table Aquifers[a]

Class of Compounds	Aerobic Water, Concentration of Pollutant (μg/L)		Anaerobic Water
	100	10	
Halogenated aliphatic hydrocarbons			
Trichloroethylene	None	None	Possible[b]
Tetrachloroethylene	None	None	Possible[b]
1, 1, 1-Trichloroethane	None	None	Possible[b]
Carbon tetrachloride	None	None	Possible[b]
Chloroform	None	None	Possible[b]
Methylene chloride	Possible	Improbable	Possible
1, 2-Dichloroethane	Possible	Improbable	Possible
Brominated methanes	Improbable	Improbable	Probable
Chlorobenzenes			
Chlorobenzene	Probable	Possible	None
1, 2-Dichlorobenzene	Probable	Possible	None
1, 4-Dichlorobenzene	Probable	Possible	None
1, 3-Dichlorobenzene	Improbable	Improbable	None
Alkylbenzenes			
Benzene	Probable	Possible	None
Toluene	Probable	Possible	None
Dimethylbenzenes	Probable	Possible	None
Styrene	Probable	Possible	None
Phenol and alykl phenols	Probable	Probable	Probable[c]
Chlorophenols	Probable	Possible	Possible
Aliphatic hydrocarbons	Probable	Possible	None
Polynuclear aromatic hydrocarbons			
Two and three rings	Possible	Possible	None
Four or more rings	Improbable	Improbable	None

[a]From Wilson and McNabb (1983) with permission of the American Geophysical Union.
[b]Possible but probably incomplete.
[c]Probable but at high concentration.

where enough historical data have been collected to define clearly the movement of a contaminant plume. The Idaho National Engineering Laboratory (INEL) is a well-studied example where there are three major classes of contaminant transport: conservative (i.e., chloride), first-order radioactive decay (i.e., tritium), and sorptive (i.e., strontium). Other case studies describing specific studies of contaminant transport and conditions are described in Chapters 6-12.

One result will, perhaps, indicate the capability of the current mathematical models. Using values of dispersivity determined from examining the distribution of chlorides in the waste plume at INEL, the movement of ^{3}H was simulated. Figure 2 is a comparison of the tritium plume as mapped from field data to the model-generated plume. In general, the match is quite good.

Recently Lewis and Goldstein (1982) compared the distribution of contaminants at INEL in October 1982 with that predicted by Robertson and Barraclough (1973). Lewis and Goldstein concluded: "The model simulations made in the early 1970s of the waste chloride and tritium plumes were approximately correct, but differed in detail, as expected, because of several conservative assumptions that tended toward 'worst case' situations."

Our general experience with mathematical model analysis is such that we can state several points with some confidence:

1. Usually the analysis of flow and transport gives reasonably good results for contaminants in which no chemical reactions (other than radioactive decay) occur. This provides some confidence in the general theory of both flow and transport.
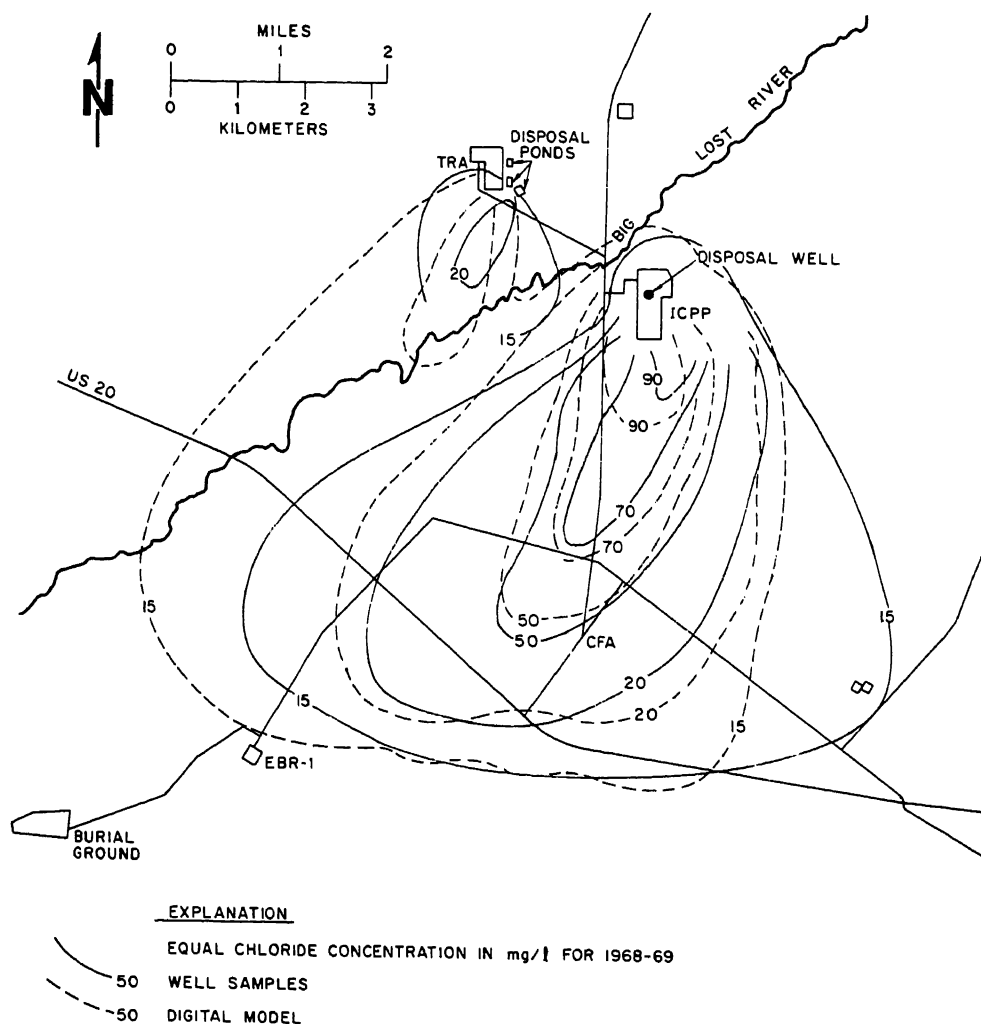
FIGURE 2 Comparison of waste chloride plumes in the Snake River Plain aquifer (at INEL) measured during 1968-1969 with that calculated using a mathematical model.

2. Simple chemical reactions such as sorption are also simulated in our analysis reasonably well.

3. Hydrodynamic dispersion as a mixing process is important.

4. The current state of the art is such that predictions of conservative contaminant movement are possible with a reasonable degree of confidence, especially for the short term—periods of a decade or perhaps several decades.

Mathematical analysis of a relatively complex transport process is well within our current capabilities, provided sufficient data are available for model calibration. This does not imply that we understand all phenomena and that further research is not necessary; the necessary research is discussed below.

RESTORATION OF CONTAMINATED AQUIFERS

The "restorability" of a contaminated area of an aquifer is highly dependent on its geologic, geochemical, and hydrologic properties and on the chemical and physical

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properties of the contaminant. In many cases, restoration is so expensive that cleanup is not considered to be economically feasible. Nevertheless, in response to public or governmental demands for positive action in cases where groundwater contamination threatens public health, aquifer cleanup programs are being required, such as at the Rocky Mountain Arsenal and more recently in "Silicon Valley" near San Jose in California where organic solvents have been found in the groundwater.

General management options currently available for restoring water quality in aquifers include the following: (1) eliminate the source of contamination but allow restoration to proceed only through natural flushing, dilution, and geochemical or biological reactions; (2) accelerate removal of contaminants through withdrawal wells, drains, or trenches; (3) accelerate flushing with artificial recharge; (4) install "impermeable" barriers to contain a contaminated area; (5) induce in situ chemical or biological reactions that would neutralize or immobilize the contaminant; and (6) excavate and remove the contaminated part of the aquifer. The selection of the best approach for a particular situation requires the ability to predict changes in flow and chemical concentration in the aquifer for each possible management alternative. This in turn requires both adequate field data to describe the aquifer systems and the development of accurate simulation models to define the groundwater flow system, the pollutant-transport mechanism, and the nature and rates of chemical, physical, and biological reactions.

The problem of cleaning up an aquifer is typified by the problems at the Rocky Mountain Arsenal near Denver, Colorado. Waste products from a chemical plant that produced chemical warfare agents and, later, insecticides leaked into a shallow aquifer. Over time these contaminants were transported toward the South Platte River by groundwater. The U.S. Department of Defense is now attempting to contain the escape of further contaminants from the Arsenal. A cleanup technique has been devised in which contaminated groundwater is pumped from the aquifer upgradient from an engineered groundwater barrier; the water is treated to reduce the concentration of the contaminants to safe levels; and the treated water is recharged to the aquifer downgradient from the barrier. The efforts at the Arsenal are described in Chapter 6, and the associated costs are described by the U.S. Army (1982).

In almost all situations, prevention of groundwater contamination is clearly much cheaper than restoration. The cost of cleanup may be so great that society may simply have to designate certain aquifers as permanently contaminated and unsuitable for further use other than for waste disposal. Virtually all the groundwater in the Earth's crust will cycle back to the biosphere; however, the time for the cycle to be completed varies enormously—from days to tens of thousands of years or even longer. In some instances, its movement is so slow that, once contaminated, groundwater will remain so more or less permanently.

CONCLUSIONS AND RECOMMENDATIONS

1. Groundwater, which is ubiquitous in the crust of the Earth, serves not only as a widely distributed source of water but as a host and transporting agent for contaminants. Scientific understanding of the chemistry and transport of contaminants in groundwater is inadequate to predict the fate of contaminants reliably.

Research is needed on the effects of chemical reactions on transport and dispersion of contaminants by groundwater and the quantification of flow in fractured media. Continued research can reduce the uncertainties associated with predicting the fate of contaminants in the subsurface. The results of such research should allow for safer disposal methods, at reduced costs. A number of the more important areas for continued scientific research are listed below.

● Continued investigation is necessary of the geochemistry of contaminant reactions in both unsaturated and saturated subsurface environments. Certain of the organic compounds appear to be especially persistent in groundwater and hazardous at low concentrations. Many, if not most, organic reactions are biologically controlled; at present the role of microorganisms is poorly understood. Only a limited number of situations and organic compounds has been investigated. Certain biological reactions might be enhanced and thereby accelerate biodegradation of contaminants.

● Increased understanding of the dispersion process in groundwater transport is important in predicting contaminant transport.

● Further research is needed into coupling chemical reactions into the transport formulation of the processes. In order for this formulation to be used, the rates of reactions must be known better than at present.

● Our understanding of groundwater flow and transport in fractured rock is elementary. There is still considerable discussion within the scientific community of the appropriate theory. Given an adequate theory, it may be possible to develop methods for measuring the appropriate parameters in the field that characterize flow and transport in fractured rocks. However, field characterization of fractured rocks is certain to be costly.

2. Even though scientific information is incomplete on the fate of contaminants in groundwater, the panel concludes that most wastes can safely be disposed of in the subsurface if repositories are selected, designed, and engineered on the basis of the nature of the wastes and adequate knowledge of the hydrology, geology, and hydrogeochemistry of the particular site. *There should be a more thorough search for disposal sites that can be used safely to isolate toxic wastes from the biosphere for long periods.*

If a policy is adopted to establish disposal sites in the vicinity of the facility generating the wastes, sites must be located that provide the necessary multiple barriers to contaminant migration. For example, the bathtub effect continues to cause troublesome problems at landfills. The solution may have to include precompaction of wastes, the construction of a good seal over the landfill, and possibly the incorporation of a controlled leak. This will involve geologic, hydrologic, and geochemical research as well as research into engineering of the disposal site and the waste form.

Deep geologic disposal is now being considered for high-level nuclear wastes. It may also have to be considered for toxic, not readily treatable, wastes. A continued search for deep waste repositories throughout the country is needed.

3. If adequate scientific understanding of the fate of contaminants in groundwater existed and suitable disposal sites and methods were identified, certain aspects of the groundwater contamination problem from the disposal of wastes would still persist. The hundreds of millions of tons of wastes generated each year could overwhelm our ability to find suitable sites. In addition, the wide variety of wastes generated from individual municipalities and industries has often, for convenience, been disposed of in the same repository; this practice complicates the prediction of the fate of these mixed wastes and the design and engineering of the repository system.

Therefore, *we recommend that a strategy be developed that provides for the segregation, treatment, and disposal of wastes according to their hazards and their chemical affinities.* In some instances recycling residual by-products may be the most cost-effective means of treating potential wastes.

Various contaminants are hazardous at different levels of concentration and behave quite differently when in the ground. Some are persistent and quite mobile; others are readily degraded and easily adsorbed. Depending on their persistence and mobility in a particular environment, different wastes should be treated and disposed of differently. Wastes can be separated into at least three different classes, each class to be disposed of in a different manner:

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I. Relatively immobile or nontoxic wastes that can be safely disposed of in the ground.

II. Wastes that can be chemically or biologically treatable or recycled. For example, some of the more toxic organic wastes can be incinerated at temperatures high enough to destroy the compounds.

III. Particularly toxic wastes that are not readily treatable, such as some of the high-level radioactive wastes, or are persistent and mobile in groundwater.

The strategy for waste disposal should require different treatment and disposal for each class of waste. For those that are relatively immobile and degrade readily (Class I above), conventional burial in a well-designed landfill is an appropriate disposal method. Wastes that are not readily treatable and are highly toxic, persistent, and mobile in groundwater (Class III wastes) would need special disposal measures (e.g., multiple-barrier schemes) such as those now being proposed for high-level nuclear wastes. The by-products of treatable wastes (Class II wastes) could conceivably be persistent and highly toxic and require special consideration. Treatment such as high-temperature incineration of certain toxic organics could greatly reduce the volume of wastes to be disposed of in the ground.

Such a strategy would certainly involve additional costs in segregating wastes. However, the cost of cleaning up a poorly designed system of disposal is usually much larger than the cost of carefully designed disposal.

4. The public must understand that use of the products of technology carries with it the responsibility for safe disposal of that technology's wastes. A pervasive difficulty with waste disposal is that individuals do not want the wastes, especially toxic wastes, disposed of in their neighborhood. However, this perception has been an important consideration in providing effective waste management.

In recognition of the need to dispose of vast quantities of waste, *governmental and industrial organizations need to agree whether various classes of wastes should be disposed of locally or in regionally designated repositories.* Wastes, especially those produced in large volumes, will probably have to be disposed of reasonably close to the location where they are generated. The quantities of many municipal and industrial wastes are such that transportation over long distances is costly. Furthermore, in the case of highly toxic wastes, transportation by rail or roadway involves risks that cannot be ignored. The nation may need to move toward a policy of requiring states to dispose of wastes within the state in which they are generated or within regions determined by interstate compacts. In Chapter 13 it is pointed out that there are efficiencies to be gained from assigning the disposal decisions to the lowest administrative level at which appropriate and reasonable decisions can be made.

In addition, in Chapter 14 it is argued that institutions must be established to examine trade-offs and to determine acceptable waste-disposal solutions that will minimize risks to society.

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I

BACKGROUND

The Extent of Groundwater Contamination in the United States

1

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The mobility of our society and the distribution of industry and agriculture depend on an available supply of clean water; nevertheless instances of groundwater contamination have been found in most sections of the country [Kerns, 1977; U.S. Environmental Protection Agency (U.S. EPA), 1980a]. For the purpose of this chapter, groundwater contamination will be defined as the addition of elements, compounds, and/or pathogens to water that alter its composition.

One of the major difficulties with groundwater contamination is that it occurs underground, out of sight. The pollution sources are not easily observed nor are their effects often seen until damage has occurred. There are no obvious warning signals such as fish kills, discoloration, or stench that typically are early indicators of surface-water pollution. Where contamination affects pumping wells, some indications may occur, although many commonly found contaminants are both colorless and odorless and occur in low concentrations. The tangible effects of groundwater contamination usually come to light long after the incident causing the contamination has occurred. This long lag time is a major problem.

Groundwater can be contaminated by a variety of compounds, both of natural origin and man-made. Contamination due to man has occurred for centuries, but industrialization, urbanization, and increased population have greatly aggravated the problem in some areas.

A contaminant usually enters the groundwater system from the land surface, percolating down through the aerated soil and unsaturated (vadose) zone. The root zone may extend 2 or 3 ft into the soil, and many reductive and oxidative biological processes take place in this zone that may degrade or biologically change the contaminants. Plant uptake can remove certain heavy metals; microbial fixation and other biological processes can

also remove a fraction of the contaminants—the size of the fraction being dependent on the nature of the contaminant.

Deeper below the root zone, which consists mainly of humus and weathered rocks, there is a reduction in such biological processes. Attenuation may occur by surface adsorption, cations in the contaminant being attracted to the negative charge on clay particles. Soils have a cation exchange capacity. Other contaminants may be removed by complexing with insoluble organic matter, which gives rise to complexed humic acids. Microbial action may influence redox potentials and cause the release of inorganic ions during decomposition (Braids, 1981). The susceptibility of different contaminants to differential attenuation varies.

Once in the aquifer, a contaminant will move with the groundwater at a rate varying between a fraction of an inch to a few feet per day, forming, under certain idealized conditions, an elliptical plume of contamination with well-defined boundaries. This dispersion process causes a spreading of the solute in a longitudinal flow direction and also transverse to the flow path (Chapter 2; Freeze and Cherry, 1979); thus the plume will widen and thicken as it travels. Attenuation of the contaminants in the aquifer may take place through dilution, volatilization, mechanical filtration, precipitation, buffering, neutralization, and ion exchange. Diffusion and dispersion will bring contaminants into contact with material that may retard their progress; thus attenuation may vary with the time and distance traveled. Unless the plume is blocked it will usually reach points of groundwater discharge such as streams, wetlands, lakes, and tidal waters (Miller, 1981). The shape of the plume will vary according to the continuity and duration of the source of contamination. Dispersion tends to dilute the contaminants; however, concentrations of contaminants are typi-

cally much higher in groundwater than in surface water (Miller, 1981).

Groundwater is a major natural resource in the United States and is often more easily available than surface water. Between 40 and 50 percent of the population depends on groundwater as its primary source of drinking water (U.S. Water Resources Council, 1978a; U.S. EPA, 1977). Groundwater delivered by community systems supplies 29 percent of the population, and a further 19 percent has its own domestic wells. About 95 percent of the rural population is dependent on groundwater for drinking purposes. Approximately 75 percent of American cities derive all or some of their supplies from groundwater (Leopold, 1974). The states vary in their dependence on groundwater. Approximately 92 percent of New Mexico's population uses groundwater for drinking water as compared with 30 percent of Maryland's population (U.S. EPA, 1977). West of the Mississippi, in the area where irrigated agriculture is prevalent, the states depend heavily on groundwater, whereas the humid eastern portions of the country are less dependent. In 1980 the fresh groundwater withdrawals for the United States totaled 88.5 billion gallons per day, of which 68 percent was used for agricultural irrigation (U.S. Geological Survey Water Information Service, unpublished data).

SOURCES OF GROUNDWATER CONTAMINATION

There are three main ways in which the chemical composition of groundwater may be changed. The first is due to natural processes. Mineralization can result from leaching, especially in arid areas. Evapotranspiration can further concentrate salts in the remaining water. In the arid southwest and southcentral areas of the United States, natural leaching has been identified as the most prevalent source of contamination (Fuhriman and Barton, 1971; Scalf et al., 1973). Chlorides, sulfates, nitrates, fluoride, and iron commonly occur in localized deposits, and their concentration in groundwater may exceed U.S. EPA standards. Arsenic and radioactivity from uranium ore also may cause local problems.

The second category of sources of contamination is that due to man's waste-disposal practices. The 1977 *Report to Congress* on waste-disposal practices and their effects on groundwater (U.S. EPA, 1977) provided estimates of the sources and the extent of groundwater contamination. At the time the report was compiled, definitive data on waste-disposal practices often were not available, and indeed this is frequently the case today. Implementation of the Resource Conservation and Recovery Act of 1976 would be expected to affect waste-disposal practices, but such recent data or estimates are not available. Sources of contamination involve all aspects of our lives, including manufacturing and service industries, agriculture, and government. It is estimated that over 30,000 chemicals are now being used and distributed through the environment and that an additional 1000 are being added each year (Weimar, 1980). Besides the 1977 *Report to Congress*, a report by the Environmental Assessment Council of The Academy of Natural Sciences of Phil-

adelphia (Pye et al., 1983) assessed the various sources of groundwater contamination. Contaminant sources from waste-disposal practices include individual sewage-disposal systems; land disposal of solid wastes; collection, treatment, and disposal of municipal wastewater; industrial and other wastewater impoundments; land spreading of sludge; brine disposal associated with the petroleum industry; disposal of mine wastes; deep-well disposal of liquid wastes; disposal of animal feedlot waste; and disposal of high- and low-level radioactive wastes resulting from a variety of activities. All of these potential sources of contamination are direct effects resulting in natural and synthetic substances entering the groundwater because of human activities (Matthess, 1982).

The third category of sources is also the direct result of human activities but is unrelated to waste-disposal practices. It includes accidental spills and leaks, agricultural activities, mining, highway de-icing salts, atmospheric contaminants and acid rain, surface water, improperly planned groundwater development leading to saltwater intrusion, and improper well construction and maintenance.

Groundwater pollution problems and their sources have been the object of numerous studies. An incomplete, but illustrative, listing would include Fuhriman and Barton (1971), Scalf et al. (1973), Miller et al. (1974), van der Leeden et al. (1975), Keeley (1976), Miller et al. (1977), U.S. EPA (1978a, 1978b, 1980a), U.S. General Accounting Office (1978, 1980); U.S. Water Resources Council (1978a, 1978b, 1978c), Jackson (1980), and Pye et al. (1983).

SEVERITY OF GROUNDWATER CONTAMINATION

In determining the overall magnitude of the national problem, defining severity poses some difficulty. The definition may be approached in several ways.

- If the contaminants in the groundwater exceed the interim standards set for drinking water, then the problem could be said to be severe, depending on the extent to which the contamination exceeds the standard, if the intended use is for drinking water. If the groundwater was not intended for drinking, then the problem need not be severe. It should be noted that the interim standards do not cover the many synthetic chemicals that can often be found in water. (See proposed rulemaking for volatile synthetic organic chemicals published in the *Federal Register*, March 4, 1982.)
- The number of persons affected by contamination might be taken into account. Thus the contamination of an aquifer in the vicinity of a municipal well field would be of more concern than contamination occurring in an isolated, sparsely populated area.
- In terms of a single aquifer, the severity of contamination may be related to the percentage of the aquifer contaminated by point or nonpoint sources.
- Nationwide, the severity of the problem may be indicated by the percentage of the available groundwater that is affected.

• A different measure of severity might be obtained if the volume of known and suspected contaminated plumes of groundwater is expressed as a percentage of the nationwide groundwater reserves.

• The degree of hazard posed by the contaminants varies according to the volume discharged, toxicity, persistence, and concentration and would be affected by how the contaminants move in the aquifer.

Thus severity could depend on one or a combination of the following parameters: concentration, persistence, and toxicity of the contaminants; the number of people affected if the contaminated aquifer is a source of drinking water; and the percentage of the available groundwater (both locally and regionally) affected by such contamination. Interwoven with each of these factors would be the economic cost of finding an alternative source of water if the contamination renders the groundwater unfit for its previous or future uses or if treatment of the water before use is not possible.

Many of the data required for these methods of assessing severity of contamination in quantitative terms simply are not available. The U.S. EPA (1980b) in the appendixes to the planning workshops to develop recommendations for a groundwater protection strategy accurately summarized the sort of information that is available from existing reports and studies, namely documentation of a large number of contamination incidents, identification of important sources of contamination, determination of the mechanisms of contamination, in-depth studies of some contamination incidents, and surveys of the number of certain contamination sources nationwide. The U.S. EPA (1980a) recognized the usefulness of conducting a nationwide survey at randomly selected sites to obtain an estimate of contamination but ruled out this possibility because of the expense of drilling and water sampling and the long time required. Instead the U.S. EPA adopted a second approach of estimating the number of sources of contamination and the amount of contamination per source. The agency obtained an order-of-magnitude estimate of the extent of the problem and utilized existing information, both qualitative and quantitative. Such assessments serve a useful purpose but only when their inherent flaws are kept in mind. Using information and estimates for only two sources of contamination—landfills and surface impoundments—and whether they are sited over usable aquifers, the length of time they have been operating, and the volume of available groundwater in storage, the U.S. EPA (1980b) estimated that between 0.1 and 0.4 percent of the usable "surface" aquifers are contaminated by industrial impoundments and landfill sites. The U.S. EPA cautioned that this is a nationwide estimate and that the two types of disposal sites used are usually found in areas of significant industrial and domestic water use and that the problem could be exacerbated by the area's dependence on groundwater. The U.S. EPA, although considering landfills and impoundments to be the most important sources, also evaluated secondary sources such as subsurface disposal systems (septic tanks) and petroleum exploration and mining and concluded that such sources had contaminated about 1 percent and 0.1 percent, respec-

tively, of the nation's usable aquifers. The U.S. EPA (1980b) therefore concluded that at present nearly 1 percent by area of the usable "surface" aquifers in the United States may be contaminated by these four activities and that the areas of contamination will increase with time. It did not include an estimate of the percentage of available groundwater contaminated by man's activities unrelated to waste disposal.

Lehr (1982) recently completed another independent estimate, assuming a total of 200,000 point sources. Using faster rates of contaminant spread over a longer period of time, Lehr considered this to be a "worst-case" estimate. He arrived at a range of between 0.2 and 2 percent. He concluded by stating that no matter how liberal or conservative the estimate, the fraction of polluted groundwater is small. This raises the question of how to determine the salience of the problem. Should contamination of 1-2 percent of our usable "surface" aquifers be considered a minor or a serious problem? Obviously, for those immediately affected, it is a serious problem. Also there are many regions where the contamination could exceed 2 percent as the contamination is not uniform geographically. Lehr (1982) optimistically predicted that the initiation of new sources of pollution from waste disposal could be eliminated in 10 yr by careful siting and facility design and operation and that by taking these steps 98 percent of our available groundwater could remain unpolluted. However, this does not mean that existing sources will not continue to produce contamination.

Little information is readily available concerning the size of the population affected by well closings due to groundwater contamination. There are well-documented cases of well closings in South Brunswick, New Jersey (Geraghty and Miller, Inc., 1979); New Castle County, Delaware (Frick and Shaffer, undated); and Long Island, New York, and California (Council on Environmental Quality, 1981). About 3 million people have been affected by well closings, both municipal and domestic, in these four states alone. Thus at present it is difficult to make useful judgments on the severity of groundwater contamination based on the number of people affected.

The types of chemicals that emanate from anthropogenic sources of contamination are varied. They range from simple inorganic ions such as nitrate (from septic tanks, feedlots, and fertilizer use), chlorides (from highway de-icing salt, saltwater intrusion, certain industrial processes), radioactive materials and heavy-metal ions (e.g., chromium from plating works) to complex organic compounds resulting from manufacturing and industrial activities and some of which are found in household cleaning fluids. The chemical composition of wastes deposited in landfills or surface impoundments is often known. Nevertheless when the constituents of such wastes interact, new compounds may be formed that would not appear on the original waste content inventory. Many industrial waste-disposal practices involve stabilization of waste, thereby rendering it less chemically active, but leachate production may still alter some of these chemicals. The degradation of contaminants by microbial organisms in the soils also changes the chemical composition, thus making it almost impossible to predict precisely what contaminants reach the aquifer.

REGIONAL ASSESSMENTS OF GROUNDWATER CONTAMINANTS IN THE UNITED STATES

In the 1970s the U.S. EPA commissioned five regional assessment reports. They summarized the geology, major aquifers, natural groundwater quality, and major pollution problems for each region. The reports were completed for Arizona, California, Nevada, and Utah (Fuhriman and Barton, 1971), the southcentral states (Scalf *et al.*, 1973), the Northeast (Miller *et al.*, 1974), the Northwest (van der Leeden *et al.*, 1975), and the Southeast (Miller *et al.*, 1977). Three additional reports were to have covered Alaska and Hawaii, the Great Lakes area, and the northcentral region, but these were not completed. The findings for the principal sources of contamination in the five regions are shown in Table 1.1. The assessment of the relative importance of the sources of contamination may have changed recently owing to a greater knowledge of the occurrence of toxic organic chemicals in groundwater. Nevertheless, at the time the U.S. EPA reports were completed, contamination resulting from natural processes unrelated to man's activities was considered to be of most concern in the arid southcentral and southwestern states. The extensive irrigation that transformed parts of the Southwest into a major crop-producing area was considered to have caused problems from irrigation return flow. Such problems would involve an increase in nitrate concentrations from fertilizer use, an increase in pesticide content, and leaching of salts. The slow rate of recharge of many of the aquifers in this area, coupled with extensive groundwater with-

TABLE 1.1 Sources of Groundwater Pollution throughout the United States and Their Prevalence in Each Region[a]

Source	Northeast	Northwest	Southeast	Southcentral	Southwest
Natural Pollution					
Mineralization from soluble aquifers				1[b]	1
Water from fault zones, volcanic origin					2
Evapotranspiration of native vegetation				2	2
Aquifer interchange					3
Groundwater Development					
Connate water withdrawal					3
Overpumping/land subsidence				1	4
Underground storage/artificial recharge	4		1	4	
Water wells	4				
Saltwater encroachment	3	4	3		1
Agricultural Activities					
Dryland farming		1			
Animal wastes, feedlots		4		3	
Crop residues, dead animals		4			4
Pesticide residues	4	3	2		4
Irrigation return flow		1		2	1
Fertilization	4	3	2		2
Mining Activities	2	2	3		2
Waste Disposal					
Septic tanks/cesspools	1	1	2	2	1
Land disposal, municipal and industrial wastes			3	2	2
Landfills	1	3	1		
Surface impoundments		2	1	3	
Radioactive waste disposal		3			
Injection wells		2		4	2
Disposal of oil-field brines				1	1
Miscellaneous					
Accidental spills	2	3	1	3	2
Urban runoff					3
Highway de-icing salts	1	4	4		
Seepage from polluted surface waters	3		4		3
Buried pipelines and storage tanks		1			
Abandoned oil and test wells	1				
Petroleum exploration and development	3		4		

[a]Northeast includes NY, NJ, PA, MD, DE, and New England; southeast: AL, FL, GA, MS, NC, SC; northwest: CO, ID, MT, OR, WA, WY; southwest: AZ, CA, NV, UT; southcentral: AR, LA, NM, OK, TX. Reports not completed for Great Lakes and North Central regions, AK, and HI.

[b]Numbers indicate degree of contamination: 1, high; 2, medium high; 3, medium low; 4, low.

drawals, has led to groundwater overdrafting and associated changes in groundwater quality and increased pumping costs. The southcentral region, the most important area for petroleum production, had a major problem with oil-field brines contaminating groundwater. Because of their sheer numbers and density, individual septic tank systems were considered the main cause for concern in the Northwest, Northeast, and Southeast. Contamination from septic tanks would result in elevated levels of nitrate. More recently, widespread use of septic tank cleaners containing degreasing agents such as trichloroethylene has resulted in groundwater contamination by synthetic organic chemicals (Council on Environmental Quality, 1981). The U.S. EPA assessments further identified the importance in the Northeast and the Southeast of problems associated with industrial development, namely leakage from buried pipelines and storage tanks and landfills and impoundments. Most of the U.S. EPA assessments were completed before the attendant publicity of Love Canal and the Valley of the Drums had made public the potential threat of such dump sites and thus spurred further investigations. All the reports were completed before the U.S. EPA's Surface Impoundment Assessment (U.S. EPA, 1978a) made available the number of such potential sources of contamination.

Keeley (1976) concluded from the U.S. EPA regional assessments that problems indigenous in one area may not occur in another but that several sources of groundwater contamination occur at a high or moderate degree of severity in each area studied. He noted that the four pollutants most commonly reported were chlorides, nitrates, heavy metals, and hydrocarbons but that this may merely be a reflection of the monitoring practices. Sampling for organic chemicals is not routine and is usually expensive, although these chemicals are almost always associated with municipal and industrial wastes. Keeley (1976) also made the point that the rank-ordered problems in the five regions were not selected on the basis of statistical information as such information was not available. The priorities were established empirically on the basis of the experience of the authorities and individuals who had worked in the five regions.

STATE SUMMARIES OF KNOWN INCIDENCES OF CONTAMINATION

Recent federally mandated surveys under the Safe Drinking Water Act have produced more information concerning the number of potential sites where groundwater contamination might occur (U.S. EPA, 1978b). In addition, many individual states have recently undertaken inventories of their groundwater contamination case histories. However, no systematic national sampling survey has been carried out, a necessary step for making an accurate appraisal and quantitative evaluation of the extent of contamination.

The Environmental Assessment Council (Pye *et al.*, 1983) conducted a survey in 1981-1982 of groundwater contamination incidents to investigate further whether additional information, collected over the last few years, could cast more light on groundwater problems in terms of severity and patterns of occurrence. Data were collected on known incidents of con-

tamination from all the states by contacting each state and requesting information on case histories of contamination if it was available. The information received varied in usefulness, some states having completed inventories and others having just started or still in the process of documentation. Several states were chosen to serve as examples in the report partly because they had the most information about case histories of groundwater contamination and because of their differing levels of industrialization, agricultural activity, population density, dependence on groundwater, and climatic conditions. The states chosen were Arizona, California, Connecticut, Florida, Idaho, Illinois, Nebraska, New Jersey, New Mexico, and South Carolina.

For the purpose of this assessment, the contaminants were divided by source rather than constituents as these were not always specified. Sources included industrial and manufacturing waste products, petroleum products, landfill leachate, chlorides, and organic wastes. Industrial and manufacturing products and wastes may be liquid or solid. Wood processing plants were included in this category. Where the wastes were specified as petroleum or its derivatives the case histories were included under that category. Petroleum products included home heating oil, aircraft fuel, and gasoline. Landfill leachate would be derived from solid, semisolid, or liquid waste of either municipal or industrial origin. Chlorides were usually designated as originating from highway de-icing salts, agricultural return flow, oil field brines, and/or saltwater intrusion. Organic wastes included those, for example, derived from plant, animal, or human wastes and those from feedlots, dairy barns, fruit and vegetable processing plants, and sewage.

The discovery of groundwater contamination is not an end in itself, and there are many remedial actions, direct and indirect, that can be taken to alleviate or reduce the problem, even though these are often costly. Direct remedial actions include actual cleanup of a contaminated site by soil removal, pumping and treating contaminated water, or artificially recharging a contaminated aquifer; preventing further spreading of contamination by building artificial barriers; and eliminating sources of contamination by removing the contaminants or closing dumping sites. Indirect remedial actions include monitoring, providing new water supplies, taking legal action, and installing filtering mechanisms to keep contaminants out of the water supply.

It should be emphasized that the case histories used in this survey only indicate the potential magnitude of the problem rather than the actual magnitude. Because the information deals only with specific incidents, it usually only provides an indication of the range and importance of point sources but not of all nonpoint sources. Where point sources were documented and known to be of importance, an analysis of them is also given.

Arizona

Arizona uses 4800 million gallons per day (mgd) of groundwater, which is 61 percent of its total water use (Fuhriman and Barton, 1971). The state is divided into five groundwater basins: the Upper and Lower Santa Cruz, White Mountain, Salt River

Valley, and Upper Salt River Basins (Arizona Division of Environmental Health Services, 1979). The Upper and Lower Santa Cruz Basins and the Salt River Valley all comprise an area known as the Basin and Range Lowlands Province, where the two major population centers of Arizona are located—Tucson and Phoenix. This area uses the most groundwater in the state and has the highest potential for contamination.

Few cases of groundwater contamination are known to have occurred—a total of 23 incidents (Arizona Division of Environmental Health Services, 1979; Hadeed, 1979; Lemmon, 1980; Robertson, 1975; Schmidt, 1972; U.S. EPA, 1981). All of them threatened or affected the water supplies. The most common source of contamination was industrial wastes (7 cases) closely followed by landfill leachate (6 cases) and human and animal wastes (6 cases). Each of the incidents involving human and animal wastes led to outbreaks of disease. The incidents were discovered, for the most part, by investigation, and in only 6 of the cases was some sort of remedial action taken.

California

California uses more groundwater than any state in the nation—approximately 13,390 mgd (California Department of Water Resources, 1975). Groundwater supplies about 40 percent of the state's water needs. The largest groundwater reservoir underlies the Central Valley Region, which occupies 10 percent of California's land area and includes the San Joaquin Valley (Thomas and Phoenix, 1976).

Overall groundwater quality is considered good and beneficial for all uses (California Department of Water Resources, 1975). There is no readily accessible complete inventory of case histories of groundwater contamination available in California, but some information on general and persistent contamination problems in the state will be summarized. The data often do not refer to specific cases of contamination but to generalized occurrences.

Six general statewide groundwater problems of present or potential concern have been identified (California State Water Resources Control Board and Regional Water Quality Control Boards, 1980):

1. Increasing nitrate concentrations from various sources are a current problem in some areas and a potential problem in other areas. Animal wastes are one potential source of nitrate contamination. In 1968, beef plus dairy cattle numbered almost 1,900,000 head, most being fed on the open range (Fuhriman and Barton, 1971). Poultry numbered 260 million, and the hog population was 150,000 head.

2. Groundwater overdrafting has resulted in seawater intrusion of the 262 coastal groundwater basins (Fuhriman and Barton, 1971), mineralization due to recirculation or percolation of used, and induced connate water migration. In the Los Angeles area, three barriers have been constructed against seawater encroachment. Overdrafting has also resulted in land subsidence, which has been most severe in the San Joaquin Valley, where subsidence in excess of 20 feet has occurred in some areas (Fuhriman and Barton, 1971).

3. Lack of officially designated hazardous-waste dump sites has resulted in illegal dumping. Many rubbish sites are not up to regulation. Fuhriman and Barton (1971) identified 207 legal sites with inadequate control over surface drainage.

4. Percolation ponds for handling industrial and military wastes are often inadequate for the types of wastes being disposed. Oil-field brines and brines from water softener regeneration plants are particularly troublesome (California Department of Water Resources, 1975).

5. Crop dusting operations have resulted in numerous sources of pesticides having potential to reach groundwater.

6. The design of proper monitoring wells may be the biggest roadblock to the process of establishing waste-discharge requirements.

Connecticut

Connecticut uses little groundwater to meet its freshwater needs—116 mgd representing 8.2 percent of its total water use (Handman et al., 1979). Nearly one third of the groundwater used (34.2 mgd) goes for public and municipal supply; the rural domestic or private well supply comes entirely from groundwater, about 49.0 mgd; 30.8 mgd is used by industry. The remaining 1.2 mgd is used for livestock, irrigation, and miscellaneous uses.

Connecticut provided details of 64 cases of groundwater contamination (Miller et al., 1974; Lindorff and Cartwright, 1977; Handman et al., 1979; Handman and Bingham, 1980; U.S. Congressional Research Service, 1980; U.S. EPA, 1981), 37 (58 percent) of which affected the water supplies. In addition, Rolston et al. (1979) mapped 450 wells known to have produced contaminated water, and Miller et al. (1974) reported that "several dozen" wells were contaminated by saltwater intrusion in the Long Island Sound area. The main reported or known contamination problem stems from industrial or manufacturing products and wastes, which account for 44 percent of the cases. The primary means of detection was by well contamination. No remedial action was reported for over 70 percent of the cases.

Florida

Florida is a major user of groundwater, requiring more than 3000 mgd in 1975 representing 18 percent of its total water use. In 1970, groundwater use was 760 mgd for public water supply, 180 mgd for rural uses, 1300 mgd for irrigation, and 710 mgd for industrial uses (Miller et al., 1977).

Florida recently completed an inventory of its known cases of groundwater contamination, and 92 cases were reported (Miller et al., 1977; Florida Department of Environmental Regulation, 1980, 1981a, 1981b; U.S. EPA, 1981). Of these, 63 percent affected or threatened water supplies. In fact, 50 percent of the cases were discovered via contamination of wells. The most important sources of groundwater contamination are chlorides from saltwater intrusion and agricultural return flow and industrial/manufacturing products or wastes, which accounted for a total of 72 percent of the cases. Of all the cases,

only 35 percent of them have had any kind of remedial action applied. At the time these data were supplied, Florida was still in the documentation phase of assessing its reported incidents of groundwater contamination.

Idaho

In 1975, Idaho used 5600 mgd of groundwater, representing 31 percent of the total water used in that state (Lehr, 1981). Fourteen percent of the total groundwater used in Idaho goes to irrigation (van der Leeden *et al.*, 1975).

There are relatively few documented case histories of groundwater contamination in Idaho (van der Leeden *et al.*, 1975; Lindorff and Cartwright, 1977; U.S. EPA, 1978a, 1981) but several potential sources of contamination to be concerned about. At the Idaho National Engineering Laboratory (INEL), located in the eastern part of the Snake River Plain, liquid-waste-disposal practices are constantly monitored, and, as of 1975, only strontium-90 has exceeded the maximum standard for drinking water (van der Leeden *et al.*, 1975). The majority of radionuclides disposed of at INEL have short half-lives and are of no consequence. Mining is another potential source of contamination. Large-scale mining goes on for silver, lead, zinc, sand and gravel, and stone. There are 11 abandoned coal mines, 1749 abandoned metal mines, and 208 abandoned non-metal mines. The extensive agricultural industry in Idaho presents several potential contamination hazards. Fertilizers and pesticides are used in large quantities. Dieldrin, now banned but once used heavily for the control of Weiss worm in potatoes, still persists in the soil. In 1973, there were 563 feedlots mostly located along the Snake River. There are at least 5000 domestic and agricultural waste-disposal wells all located in the Snake River Plain. A few cases of serious contamination from waste-disposal wells have resulted because of the high permeability of the aquifer. Of the 29 known incidents, the majority (14 or 48 percent) are due to contamination from human and animal organic wastes. Industrial and radioactive wastes combined account for 24 percent of the cases. Of the incidents, 62 percent actually affected the water supplies and 34 percent threatened them. Thirty-one percent of the contamination incidents resulted in or posed the threat of outbreaks of disease. The means of detection was usually by well contamination or by investigation. In 55 percent of the cases no mention was made of any remedial action that has been taken.

Illinois

In Illinois, groundwater is the freshwater source for approximately 1600 public water-supply systems and the principal source for industry, agriculture, and almost all private water-supply systems in the state (Gibb and O'Hearn, 1980). The state used about 1000 mgd of groundwater in 1978, which accounted for about 8 percent of total freshwater use. In 1970, 38 percent of the entire state population and 82 percent of the rural population were dependent on groundwater as a drinking source (Piskin *et al.*, 1980).

Fifty-eight cases of contaminated groundwater have been documented for Illinois (Walker, 1969; Lindorff and Cartwright, 1977; Piskin *et al.*, 1980; U.S. Congressional Research Service, 1980; U.S. EPA, 1981). Of the known incidents of groundwater contamination, 44 of them (76 percent) affected or threatened the water supplies. The most prevalent source of contamination is from animal and human wastes (20 cases or 34 percent) followed by industrial waste and landfill leachate (21 and 28 percent, respectively). Groundwater from shallow wells often has large concentrations of nitrate. Eighty-one percent of the dug water wells, less than 50 feet deep, contained in excess of the standard of 10 mg/L of NO_3-N_2, as opposed to 34 percent of the deeper drilled wells in Washington County (National Research Council, 1977). All the incidents involving contamination from animal or human wastes affected or threatened the water supplies. The majority of incidents (45 or 78 percent) were detected by well contamination, investigation, and outbreaks of illness. Illinois has a good record for applying remedial actions, as 66 percent of the incidents have received some sort of action.

There are no documented cases of groundwater contamination from waste-injection wells, but they are potential hazardous sources of contamination (Ford *et al.*, 1981). In Illinois, there are 9 Class I wells (the deepest variety, injecting below the deepest underground source of drinking water) and 17,167 Class II wells, which are oil- and gas-related, enhanced-recovery, brine-injection, and liquid-hydrocarbon storage wells.

Nebraska

This predominantly agricultural state uses nearly twice as much groundwater as Florida, 5900 mgd or 68 percent of its total water supply (Lehr, 1981). Most of this is supplied by the extensive Ogallala Aquifer, which underlies parts of Texas, New Mexico, Oklahoma, Kansas, Colorado, Nebraska, Wyoming, and South Dakota. Of the 35 incidents of contamination from point sources, 34 percent threatened or affected the water supplies (Engberg and Spalding, 1978; Spalding *et al.*, 1978a, 1978b, 1979; Exner and Spalding, 1979; Gormley and Spalding, 1979; Junk *et al.*, 1980; Nebraska Department of Environmental Control, 1980a, 1980b, 1981; Spalding and Exner, 1980; University of Nebraska, 1980; U.S. EPA, 1981). Incidents involving pesticides and fertilizers accounted for 43 percent of the cases, but these compounds are also involved in nonpoint-source contamination. The second most prevalent sources of contamination are plant, animal, and human wastes, accounting for 31 percent. Most of the incidents were discovered following investigation, and in 74 percent of the cases no remedial action was reported.

Various surveys in Nebraska sampled 4350 wells and found that 700 contained NO_3-N_2 contamination in excess of the standard of 10 mg/L. Studies showed that of the contaminated wells 575 (82 percent) were contaminated by nonpoint sources such as nitrogen fertilizer contained in irrigation return flow. Septic tanks, barnyards and feedlots, and point sources accounted for the remaining 18 percent.

New Jersey

New Jersey, one of the most densely populated regions in the United States, has more than 16,000 potable wells (Tucker, 1981). Sixteen percent of the drinking water is derived from underground sources. In the southern half of the state, more than 90 percent of the population receives its drinking supply from groundwater. In 1976 it was estimated that 406 mgd of groundwater went to public supply, 75 mgd to rural supply, 118 mgd to industry, and 53 mgd to irrigation—a total of 652 mgd or 54 percent of the total freshwater supply used in New Jersey.

In 1981 New Jersey completed an extensive sampling of its groundwater aquifers for toxic chemical contamination and, in addition, compiled a comprehensive inventory of groundwater contamination cases—374 incidents (New Jersey Department of Environmental Protection, 1981). The aquifer samples for chemical analysis were collected from a random sampling of wells throughout the state—a sampling, however, designed to cover all the different areas. Where problems were found, additional investigations of potential sites of contamination in the same area were conducted. The contamination inventory lists all known groundwater pollution in the state but may be incomplete owing to the occurrence of new cases. The most numerous incidents are those involving industrial wastes and petroleum products, which accounted for 40 and 39 percent of the cases, respectively. Pesticides account for few of the cases, even though New Jersey is both an industrial and agricultural state. In 41 percent of the cases some form of remedial action has been taken; in 48 percent, remedial action is being considered or a monitoring program has been started.

New Mexico

Groundwater provided 49 percent of New Mexico's water in 1970; 85 percent of the groundwater withdrawals were used for irrigation (Scalf et al., 1973). In 1975, groundwater usage increased slightly, accounting for 50 percent of the total water usage or 1600 mgd.

Groundwater quality is threatened by overpumping in the eastern part of the state; mining for uranium, copper, molybdenum, and potash in various areas throughout the state; and oil production in the northeastern and southwestern parts of the state.

There have been 105 reported incidents of groundwater contamination in New Mexico (New Mexico Environmental Improvement Division, 1980; U.S. EPA, 1981). Most are cases of chloride contamination from oil-field brines (40 cases). Of these cases, 36 affected water supplies. Animal and human wastes accounted for 31 cases, 28 of which resulted in contaminated drinking water supplies. Mine wastes also accounted for 14 incidents. Only 6 percent of the total reported incidents caused adverse public health effects. The majority of incidents were discovered by contamination of well water. Fewer than 30 percent of the cases of groundwater contamination mentioned that any remedial action had been taken.

South Carolina

In 1970, 61 percent of the total population of South Carolina relied on groundwater for their drinking water supply (Scalf et al., 1973), and groundwater accounted for 23 percent of the total water usage from all sources. Lehr (1975), however, showed that in 1975 only 3 percent of the total use was attributable to groundwater. Total groundwater usage in 1975 was 200 mgd. There are 89 known cases of groundwater contamination (South Carolina Department of Health and Environmental Control, 1980, 1981). Petroleum products are involved in the majority of incidents, 43 cases (48 percent), of which 88 percent affected the water supply. Contamination by industrial wastes accounted for 28 of the incidents (31 percent), of which half threatened or affected the water supply. More than half the cases were detected by well contamination. For the majority of incidents (89 percent) remedial action was under consideration, monitoring had been started, or no remedial action was mentioned.

SUMMARY AND CONCLUSIONS

The summaries of groundwater pollution sources completed by the U.S. EPA (Table 1.1) and the Environmental Assessment Council (EAC) (Table 1.2) show that contamination problems from several sources have been reported from all parts of the United States and that the problems vary from one region to another, depending on climate, population density, intensity of industrial and agricultural activities, and the hydrogeology of the region. A comprehensive national survey might well uncover other important sources of contamination or different frequencies of the same sources. Neither the U.S. EPA nor the EAC summaries can be considered complete as they do not result from comprehensive national surveys. It is difficult to estimate severity from these summaries as there is no established method for doing so. Essentially the information contained in the EAC state summaries presents a "best-case" scenario; the situation can only change as new cases of contamination are discovered.

The important sources of contamination identified in the EAC state summaries (Table 1.2) differ somewhat in order of importance from those identified by the U.S. EPA summaries (Table 1.1) partly because the EAC summarized information from individual states whereas the U.S. EPA did regional summaries and because the methods of assessment were different. The U.S. EPA summaries are empirical assessments relying on the expertise of professionals who had worked in the regions studied (J. W. Keeley, Kerr Environmental Research Laboratory, personal communication, 1982). Data for the EAC state summaries were based on anecdotal reports of case histories supplied by state agencies, and the categories for types of contaminants are fewer and broader than those in the U.S. EPA surveys.

Some generalizations can be made from the combined results of the two surveys. It is clear that human and sometimes animal wastes are a high-priority source of contamination throughout

TABLE 1.2   Most Frequently Reported Sources of Groundwater Contamination in the Ten States Reviewed by the Environmental Assessment Council[a]

	Groundwater Use, mgd[b]	Natural Quality of Groundwater[c]	Most Frequently Reported Sources of Contamination	Total Number of Known Contamination Incidents	% Affecting or Threatening Water Supply	% For Which Remedial Actions Have Been Undertaken
Arizona	4800	Generally good; mineralization problems	1. Industrial wastes 2. Landfill leachate 3. Human and animal wastes	23	100	26
California	13400–19000	Good	1. Saltwater intrusion 2. Nitrates from agricultural practices 3. Brines and other industrial and military wastes	Not known	Not known	Not known
Connecticut	116	Good to excellent	1. Industrial wastes 2. Petroleum products 3. Human and animal wastes	64	59	30
Florida	3000	Generally good	1. Chlorides from saltwater intrusion and agricultural return flow 2. Industrial wastes 3. Human and animal wastes	92	63	39
Idaho	5600	Good	1. Human and animal wastes 2. Industrial wastes 3. Radioactive wastes	29	97	45
Illinois	1000	Generally good	1. Human and animal wastes 2. Landfill leachate 3. Industrial wastes	58	76	70
Nebraska	5900	Generally good	1. Irrigation and agriculture 2. Human and animal wastes 3. Industrial wastes	35	34	26
New Jersey	790	Generally good	1. Industrial wastes 2. Petroleum products 3. Human and animal wastes	374	50	41
New Mexico	1500	Fair to good; mineralization problems	1. Oil-field brines 2. Human and animal wastes 3. Mine wastes	105	83	29
South Carolina	200	Suitable for most uses	1. Petroleum products 2. Industrial wastes 3. Human and animal wastes	89	74	45

[a]Pye *et al.* (1983).
[b]Lehr (1981).
[c]van der Leeden *et al.* (1975), Miller *et al.* (1974, 1977), Fuhriman and Barton (1971), and Scalf *et al.* (1973)

the country. In the EAC survey, human and animal wastes are among the top three contaminants in every state surveyed except California (for which individual cases were not available). Human wastes are ranked as highest-priority contaminants in three of the regions surveyed by the U.S. EPA— Northeast, Northwest, and Southwest. They are of medium-high priority in the southeastern and southcentral regions. Industrial wastes are also common and high-priority contaminants in most regions of the country. In the Northeast, both surveys show industrial waste disposal as the biggest source of groundwater contamination. In the southeastern (Florida, South Carolina) and northwestern (Idaho) states surveyed by EAC, industrial wastes are the second most prevalent contaminants of groundwater, which concurs with the U.S. EPA regional survey. And in the northcentral states (Illinois, Nebraska), where agricultural activities are important, industrial wastes are ranked third in reported frequency of contamination. In the southwestern (Arizona, California) and southcentral (New Mexico) states, disposal of oil-field brines accounts for a high percentage of industry-related contamination. Land disposal of general industrial wastes is of secondary importance.

Beyond industrial wastes and human and animal wastes, the sources of contamination vary considerably from one region of the country to another depending on the intensive activities of a particular state (e.g., mining, agriculture, industry) and the geographic and geologic location of the state (some coastal states have severe problems with saltwater intrusion into groundwater; states located in snowbelts have problems with chloride

contamination from road salts; states having soluble aquifers have problems with mineralization). The major sources of contamination are nearly all induced by human activity, apart from naturally poor quality water caused by dissolution of natural compounds in the strata through which groundwater flows.

Although contamination of groundwater has occurred throughout the United States, and is likely to continue to some extent in the future, we are still in a position to make choices on how best to use, manage, and protect this valuable resource.

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II

PROCESSES

Movement of Contaminants in Groundwater: Groundwater Transport— Advection and Dispersion

2

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INTRODUCTION

The relative success of attempts to model a process is a measure of how well it is understood. A first level of understanding produces a conceptual model and a higher level of understanding results in a quantitative model. Failure to understand dispersion in porous media at a level necessary for constructing reliable mathematical models has impeded progress in studying contaminant transport in groundwater. However, within the past 5 years there have been many attempts at improving our understanding of the nature of dispersion in porous media. As a result there has been significant progress in refining contaminant transport models. Some of this progress as well as background information on dispersion in porous media is reviewed in this chapter.

Dispersion in porous material refers to the spreading of a stream or discrete volume of contaminants as it flows through the subsurface. For example, if a spot of dye is injected into porous material through which groundwater is flowing, the spot will enlarge in size as it moves downgradient. More specifically, in a three-dimensional cartesian coordinate system where the average groundwater velocity is parallel to the x axis, a sphere of dye moving horizontally along the x axis will undergo longitudinal spreading or dispersion parallel to the x axis and transverse dispersion parallel to the y and z axes.

Dispersion causes mixing with uncontaminated groundwater, and hence dispersion is a mechanism for dilution. Moreover, dispersion causes the contaminant to spread over a greater volume of aquifer than would be predicted solely from an analysis of groundwater velocity vectors. This spreading effect will be of particular concern when toxic or hazardous wastes are involved. Dispersion is chiefly of importance in predicting

transport away from point sources of contamination but is also influential in the spread of nonpoint-source contaminants, although of lesser importance. Contaminants introduced into the subsurface from nonpoint sources will be spread over a relatively large area because of the nature of the loading pattern. In this case, dispersion merely causes a relatively large zone of contaminated water to acquire some rough fringes. Dispersion is of interest because it causes contaminants to arrive at a discharge point (e.g., a stream or a water well) prior to the arrival time calculated from the average groundwater velocity. The accelerated arrival of contaminants at a discharge point is a characteristic feature of dispersion that is due to the fact that some parts of the contaminant plume move faster than the average groundwater velocity.

Dispersion is caused by both microscopic and macroscopic effects. Mechanical dispersion on a microscopic scale (Figure 2.1) is a result of deviations of velocity on a microscale from the average groundwater velocity. These velocity variations arise because water in the center of a pore space travels faster than the water near the wall and because diversion of flow paths around individual grains of porous material causes variations in average velocity among different pore spaces. These two factors create mechanical dispersion on a microscopic scale. In addition, it is customary to include molecular diffusion as a component of microscopic dispersion. Molecular diffusion occurs as species move from higher to lower concentrations. Thus, microscopic dispersion includes the effects of mechanical dispersion and molecular diffusion.

One of the first field and laboratory investigations of dispersion in porous media was performed by Slichter (1905). He obtained S-shaped breakthrough curves (concentration versus time curves), which are characteristic of flow affected by dis-

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FIGURE 2.1   Microscopic dispersion (adapted from Freeze and Cherry, 1979).

persion, during field tracer tests that he performed for the purpose of estimating groundwater velocity. He correctly attributed the effect to dispersion:

The writer formerly supposed that the gradual appearance of the electrolyte at the downstream well was largely due to the diffusion of the dissolved salt, but it is now evident that diffusion plays but a small part in the result. The principal cause of the phenomena [sic] is now known to be due to the fact that the central thread of water in each capillary pore of the soil moves faster than the water at the walls of the capillary pore, just as the water near the central line of a river channel usually flows faster than the water near the banks. . . . Owing to the repeated branching and subdivision of the capillary pores around the grains of the sand and gravel, the stream of electrolyte issuing from the well will gradually broaden as it passes downstream. The actual width of this charged water varies somewhat with the velocity of the ground water. . . . (Slichter, 1905, p. 23).

In subsequent laboratory experiments Slichter (1905, p. 41) studied the phenomenon more carefully and concluded that "the spread of the electrolyte, as shown by these experiments, is not to be explained by the diffusion of the salt, but must be explained by the continued branching and subdivision of the capillary pores around the individual grains of the sand."

In fact, some of the dispersion observed by Slichter in field studies was probably a result of macroscopic dispersion. On a macroscopic scale, dispersion is caused by the presence of large-scale heterogeneities within the subsurface. For example, Skibitzkie and Robinson (1963) demonstrated that lenses of high-permeability material within a matrix of lower permeability caused the spreading of streams of dye as water and dye moved through a tank filled with sand (see Figure 2.2). It is now generally recognized that the presence of heterogeneities in the subsurface, rather than microscopic dispersion alone, is responsible for the appreciable spreading of contaminants documented in a number of field studies (e.g., Anderson, 1979).

Pioneering theoretical work on dispersion was done by Taylor (1921, 1953), and serious efforts at applying modified forms of this theory to field studies involving the transport of contaminants in groundwater have been under way since the early 1970s. However, there is still considerable uncertainty concerning methods for quantifying dispersion and for measuring dispersion in the field. To some extent this uncertainty has impeded progress in developing reliable contaminant-transport models. However, within the past 5 yr there has been much effort and some progress in quantifying macroscopic dispersion. These efforts are reviewed below.

ADVECTION-DISPERSION EQUATION

Most attempts at quantifying contaminant transport have relied on a solution of some form of a well-known governing equation referred to as the advection-dispersion equation. Advection refers to the transport of contaminants at the same speed as the average linear velocity of groundwater (v), where

$$v = Kl/n \qquad (2.1)$$

and K is hydraulic conductivity, I is the head gradient, and n is effective porosity. The velocity defined by Eq. (2.1) has also been called the average pore velocity. The nomenclature used here (i.e., average linear velocity) was introduced by Freeze and Cherry (1979). Moreover, the term *advection* is used here in preference to the term *convection* because convection often carries the connotation of transport in response to temperature-induced density gradients.

The advection-dispersion equation is derived by combining a mass-balance equation with an expression for the gradient of the mass flux (see Bear, 1972; Wang and Anderson, 1982). The

FIGURE 2.2   Macroscopic dispersion (adapted from Skibitzkie and Robinson, 1963).
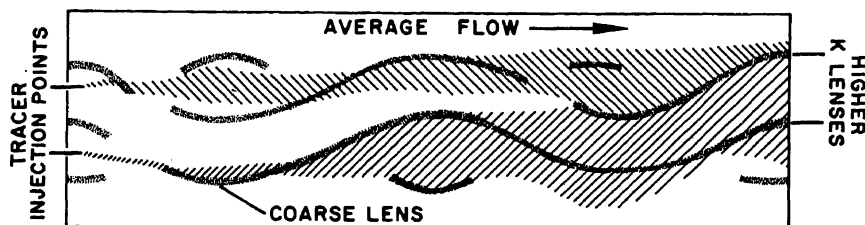
difficulties in quantifying dispersion are related to the fact that field studies of flow through porous media are by necessity conducted at a macroscopic rather than a microscopic level. For example, Darcy's law, the fundamental equation for describing flow through porous media, is a macroscopic equation. That is, K, I, and n in Eq. (2.1) are measured in some representative elementary volume (REV), and these values are assumed to represent an average of K, I, and n within the REV. Likewise, spatial averaging is routinely done when deriving the advection-dispersion equation. Fried (1975) noted that "The basis of dispersion theory is a *measurement* problem. . . . Theoretical macroscopic concentration, for instance, which appears in mathematical models, should correspond to the experimental concentration; this is not simple. . . ."

The standard approach in analyzing dispersion, which is embodied in the advection-dispersion equation, is to use an average linear velocity. A number of investigators maintain that this approach is reasonable because it will never be practical to define the velocity field in detail.

The key assumption in deriving a term to represent dispersion is that dispersion can be represented by an expression analogous to Fick's second law of diffusion:

$$\text{mass flux due to dispersion} = \frac{\partial}{\partial x_i}\left(D^*_{ij}\frac{\partial c}{\partial x_j}\right), \quad (2.2)$$

where c is concentration and D^*_{ij} is the coefficient of dispersion (the i, j indices refer to cartesian coordinates). The coefficient of dispersion can be shown to be a second-rank tensor, where

$$D^*_{ij} = D_{ij} + D_d. \quad (2.3)$$

Then, D_{ij} is the coefficient of mechanical dispersion and D_d is the coefficient of molecular diffusion (a scalar). An effective diffusion coefficient is generally taken to be equal to the diffusion coefficient of the ion in water (D_d) times a tortuosity factor. The tortuosity factor has a value less than 1 and is needed to correct for the obstructing effect of the porous medium. Effective diffusion coefficients are generally around 10^{-6} cm²/sec, although a range of 10^{-5} to 10^{-7} cm²/sec is not inconceivable (Grisak and Pickens, 1981). Except for systems in which groundwater velocities are very low, the coefficient of mechanical dispersion generally will be one or more orders of magnitude larger than D_d. Therefore, in many practical applications the effects of molecular diffusion may be neglected ($D_d = 0$). The coefficient of mechanical dispersion is routinely taken to be the product of the magnitude of the velocity vector times a parameter known as dispersivity, which is commonly and somewhat vaguely referred to as a characteristic mixing length.

The advection-dispersion equation in its most general form is written

$$\frac{\partial}{\partial x_i}\left(D^*_{ij}\frac{\partial c}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(cv_i) - \frac{c'W}{n} + \sum_{k=1}^{s} R_k = \frac{\partial c}{\partial t},$$

$$\underset{\text{dispersion term}}{} \quad \underset{\substack{\text{advection}\\\text{term}}}{} \quad \underset{\substack{\text{sink/source}\\\text{term}}}{} \quad \underset{\substack{\text{chemical-reaction}\\\text{term}}}{} \quad (2.4)$$

where c' is the concentration of solute in a source or sink fluid, and W is the volume flow rate of the sink or source fluid per unit volume of porous material. In the chemical-reaction term, R_k is the rate of production of the solute in reaction k of s

different reactions. The problems involved in quantifying the chemical-reaction term are discussed in Chapter 3 of this report.

If the advection-dispersion equation is to be used to evaluate dispersion in groundwater systems, two questions must be addressed:

1. Is it valid to assume that the dispersion component of Eq. (2.4) can be represented by a form of Fick's law [Eq. (2.2)]?
2. Can dispersivity be defined in terms of physically measurable parameters?

IS DISPERSION A FICKIAN PROCESS?

Much of the theory on which the analysis of dispersion in porous material and in rivers is based stems from the pioneering work of Taylor (1921, 1953), who suggested that dispersion could be represented as a Fickian process. This assumption as applied to porous media has since been questioned by several researchers. Fried (1975, pp. 17-27) cites several examples of laboratory experiments in which the experimental results did not fit theoretical curves derived from solutions of the advection-dispersion equation, and Dagan (1982) noted that "there is no *a priori* reason to believe that the diffusion type equation is valid at all" for contaminant transport through porous media.

Taylor and others (e.g., Fischer, 1973) who continued the development of the theory of dispersion clearly recognized that the Fickian assumption is valid only after a certain length of time has elapsed in which the dispersion process develops. A procedure for predicting the length of this initial development period has not yet been perfected. Indeed, until recently it was not recognized that for the heterogeneous systems encountered in the field this development process requires substantial transport from the source. For example, some researchers believe that dispersion becomes Fickian only at distances on the order of 10s to 100s of meters from the source in porous media (Matheron and DeMarsily, 1980; Gelhar and Axness, 1981; Dagan, 1982) and on the order of kilometers in rivers (Beltaos and Day, 1978). Furthermore, in certain hydrogeologic settings dispersion may never become Fickian (Matheron and DeMarsily, 1980; Smith and Schwartz, 1980).

After the initial development period, that is when dispersion has become Fickian, the concentration distribution and concentration-time profiles should behave according to particular solutions of Eq. (2.4). Specifically, the solution for instantaneous release of a contaminant from a point source predicts that concentration-distance curves will approximate a Gaussian distribution except for short times [Figure 2.3(a)]. However, concentration-time curves are typically skewed on the right except for long times or large distances from the source [Figure 2.3(b)].

The problems in applying Taylor dispersion theory to rivers are discussed in some detail by Beltaos and Day (1978). Most concentration-time curves obtained from tracer studies in rivers are skewed on the right, and Gaussian curves are rare (Day and Wood, 1976). Beltaos and Day (1978) noted that concentration-time curves in the Lesser Slave River deviated less from

SPATIAL DISTRIBUTION

DISTANCE

(a)

TEMPORAL DISTRIBUTION

TIME

(b)
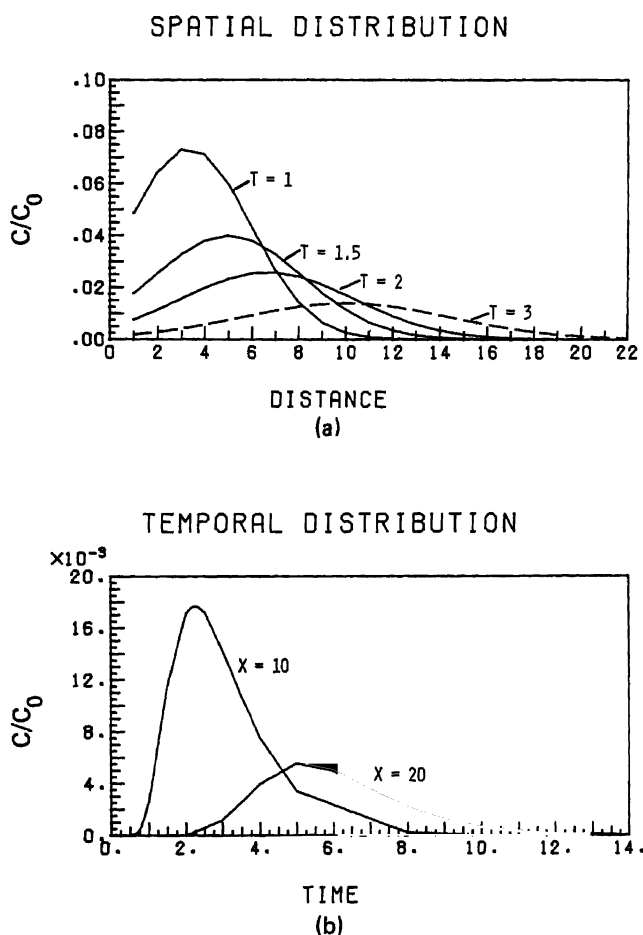
FIGURE 2.3   (a) Concentration distribution in space; (b) concentration-time curves. C/C_0 is a dimensionless concentration. The dimensions of distance and time and other variables and parameters are any consistent set of units (e.g., distance in meters, time in days, and velocity in meters/day). In this example, velocity and longitudinal dispersivity were set equal to 1.0 and transverse dispersivities were 1/20.

the Gaussian than did several mountain streams studied by Day (1975) and concluded that the Lesser Slave River is less "irregular" in that it deviates less from prismatic laboratory flumes where Gaussian curves are normally obtained relatively quickly. They also demonstrated that concentration-time curves for this river approximated Gaussian curves at a distance of about 14 km from the tracer release point. However, the growth of the variance of the concentration distribution during the non-Gaussian period did not follow a Fickian model. If dispersion is a Fickian process, then the variance of the concentration distribution should increase linearly with time or distance, and the longitudinal dispersion coefficient and the dispersivity will be a constant for constant velocity. However, the variance of the concentration distribution in the rivers considered by Beltaos and Day (1978) increased with the square of the distance and the dispersion coefficient, and the dispersivity also increased with distance for constant velocity. Based

on these analyses it appears that the initial development period of non-Fickian behavior may be long for many rivers.

Similar behavior has been predicted for porous media on the basis of theoretical studies (Gelhar et al., 1979; Matheron and DeMarsily, 1980; Dagan, 1982). Specifically, for long times or large travel distances, dispersion in some geologic settings can be accurately represented as a Fickian process. However, under certain conditions (e.g., flow parallel to bedding where lateral dispersion across bedding planes is negligible) theoretical studies suggest that the Fickian limit (also known as the Taylor limit) may never be reached and dispersion may never become Fickian (Mercado, 1967; Gelhar et al., 1979; Matheron and DeMarsily, 1980). Similarly, Smith and Schwartz (1980), who conducted many numerical experiments of hypothetical aquifers, found that for most of the situations that they modeled the variance of the concentration distribution was highly irregular and did not approximate a Gaussian distribution within the lengths of the simulated flow paths.

Field evidence to corroborate these theoretical findings for porous media is sparse. Results from a field tracer test described by Sudicky and Cherry (1979) suggested that the concentration patterns were somewhat irregular near the source of the tracer but became approximately Gaussian farther downgradient. An analysis of the variance of the concentration distribution by Sudicky and Cherry (1979) indicated that the growth of the variance was nonlinear and the dispersivity increased with distance. Several other investigators (Molinari et al., 1977; Lee et al., 1980; Pickens and Grisak, 1981a, 1981b) also noted an increase in dispersivity with distance from the tracer source, which indicates that dispersion was not Fickian within the distances in which the measurements were taken (see Figure 2.4).

DEFINITION OF DISPERSIVITY

Contaminant transport models usually have been applied to existing waste-disposal sites where a contaminant plume had been identified during a field monitoring program. The standard modeling procedure has been to adjust values of dispersivity until the model correctly reproduces the observed concentration distribution. Anderson (1979), among others, noted that dispersivity values used in most applications of contaminant transport models through 1979 were calibration (or fitting) parameters. Values in the range of 3 to 200 m have been reported (see Anderson, 1979), but these values may not be physically meaningful. In order to obtain meaningful predictions of contaminant movement at existing sites and to apply advection-dispersion models to new or proposed sites, an accurate way of quantifying dispersivity needs to be developed.

Results from theoretical studies suggest that dispersion is non-Fickian near the source of the contaminant but that dispersion generally becomes Fickian at large times or travel distances, when a constant dispersivity value is achieved. Therefore, for large times, it should be possible to use the standard form of the advection-dispersion equation [Eq. (2.4)] if the dispersivity parameter in the coefficient of mechanical dispersion can be evaluated in terms of parameters that can be measured in the field.
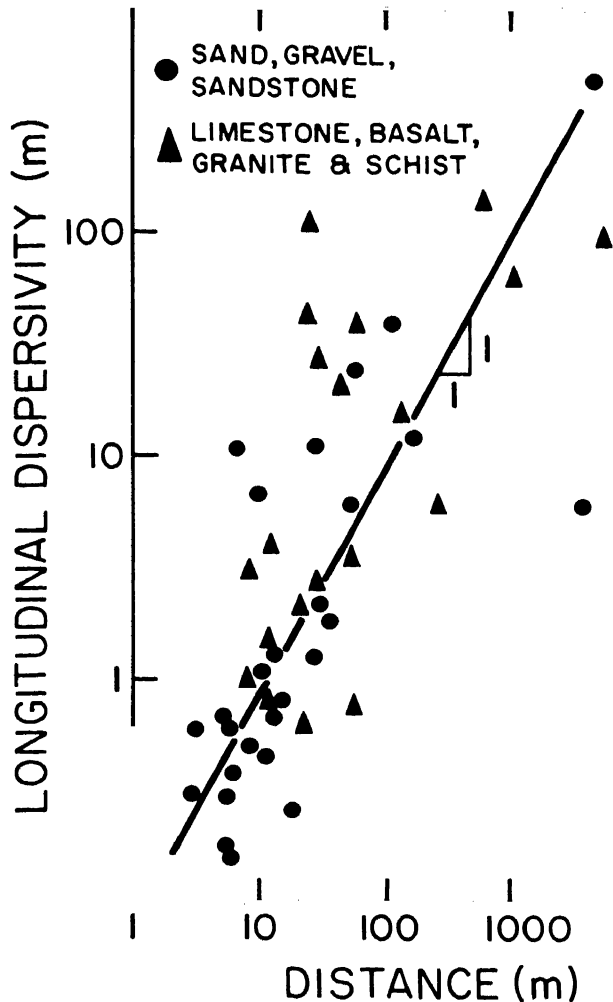
FIGURE 2.4   Variation of dispersivity with distance (adapted from Lallemand-Barres and Peaudecerf, 1978).

Gelhar *et al.* (1979) showed that near the source, dispersivity steadily increases with distance and at the Taylor limit approaches an asymptotic value. Gelhar *et al.* (1979) and Gelhar and Axness (1981, 1983) derived a variety of expressions for evaluating the asymptotic longitudinal and transverse dispersivities. In their analyses, the asymptotic dispersivity is expressed in terms of various statistical properties of the hydraulic conductivity distribution. For example, for the perfectly stratified aquifer considered by Gelhar *et al.* (1979), the asymptotic value for the longitudinal dispersivity is $\alpha_L + A_\infty$, where

$$A_\infty = \frac{1}{3\alpha_T} (\sigma_k \, l/\overline{K})^2, \tag{2.5}$$

where σ_K is the standard deviation of the log normal hydraulic conductivity distribution; l is a correlation length, and $\overline{K}$ is the mean hydraulic conductivity. The parameters α_L and α_T are, respectively, the local longitudinal and transverse dispersivities defined at the level of the representative elementary volume (REV) used in the spatial averaging that is routinely done when

deriving the advection-dispersion equation. Local dispersivities are on the order of 10^{-2} to 1 cm for laboratory experiments and range from 10^{-1} to 10^2 m for tracer tests in the more heterogeneous porous material typically encountered in the field (see Klotz *et al.*, 1980). However, it is likely that some of the dispersivities calculated on the basis of field tracer tests are biased by the so-called scale effect (see Figure 2.4). That is, because dispersivity increases with distance from the injection point, some of the values reported from tracer tests are too high to be representative of local dispersivities and in fact are equivalent dispersivities that represent dispersion between the measuring point and the injection point. Typical values for the local longitudinal dispersivity are probably on the order of 10^{-2} to 1 m (Gelhar *et al.*, 1979; Matheron and DeMarsily, 1980; Gelhar and Axness, 1981). Transverse dispersivity is smaller than longitudinal dispersivity; ratios of longitudinal to transverse dispersivity on the order of 10 to 100 have been suggested (see Anderson, 1979).

According to the general three-dimensional analysis of Gelhar and Axness (1981), dispersivity is a second-rank symmetric tensor (A_{ij}). Their result is in contrast to the somewhat alarming finding of de Josselin de Jong (1968), who concluded that dispersivity is a tensor of infinite rank in the anisotropic case. Gelhar and Axness (1981) showed that in the general three-dimensional case with random orientation of stratification, the longitudinal dispersivity is $\alpha_L + A_{11}$, where

$$A_{11} = \sigma_k^2 \lambda_*/\gamma^2 \tag{2.6}$$

and λ_* is a correlation scale; γ is a mean flow parameter that can be approximated by $1 + \sigma_K^2/6$ for small values of σ_K^2 or $\exp(\sigma_K^2/6)$ for large σ_K^2. Gelhar and Axness (1981) also present more involved expressions for the other components of A_{ij}.

Matheron and DeMarsily (1980) analyzed dispersion for the case of two-dimensional flow through a stratified aquifer. According to their analysis the magnitude of the asymptotic longitudinal dispersivity is dependent on the magnitude of the ratio of vertical to horizontal velocities. As this ratio increases, the asymptotic dispersivity becomes small. They were pessimistic about predicting the asymptotic dispersivity *a priori* because the value will change with changes in the flow field. Gelhar and Axness (1981) analyzed three-dimensional dispersion in a stratified aquifer, and their expression for longitudinal dispersivity was also dependent on a mean flow parameter as is Eq. (2.6). However, they suggest that the mean flow parameter (γ) can be expressed in terms of the variance of the hydraulic conductivity distribution. Dagan (1982) showed that for a porous media having a three-dimensional isotropic but heterogeneous structure, the asymptotic value for the dispersivity is equal to $l\sigma_K^2$, where l is the length characterizing the exponential autocorrelation of the natural logarithm of the hydraulic conductivity and σ_K^2 is the variance of the natural logarithm of the hydraulic conductivity.

For large times or large distances it may be possible to use expressions like Eqs. (2.5) and (2.6) to calculate values for dispersivity for use in the advection-dispersion equation. If dispersion does in fact become Fickian at large times or distances, a key question is: What is the length of time that must

elapse before the advection-dispersion equation is applicable and expressions such as Eqs. (2.5) and (2.6) are valid? Matheron and DeMarsily (1980) found that for a typical set of aquifer parameters, the Taylor limit would be reached after 140 days and 600 m of travel. Gelhar and Axness (1981) and Smith and Schwartz (1980) also suggested that the Taylor limit will not be reached until the contaminant has traveled on the order of tens or hundreds of meters from the source. According to a theoretical analysis by Dagan (1982), dispersion should be Fickian at a distance from the source approximately equal to $50L$, where L is the integral scale of the natural logarithm of the hydraulic conductivity distribution. For two-dimensional flow fields, L may be hundreds to thousands of meters, but for three-dimensional analyses L is expected to be on the order of meters.

While there has been much progress in defining dispersivity at large distances from the source, no clear consensus has emerged regarding the appropriate way to quantify dispersion near the source before the Taylor limit is reached. Gelhar et al. (1979) derived a revised form of the advection-dispersion equation, which includes several additional terms of higher order that are required to represent dispersion close to the source. They then analyzed the development of the dispersion process for early times and showed that the definition of the time-dependent dispersivity requires evaluation of an integral for which the small time limit for the case of one-dimensional flow through a stratified aquifer is $\alpha_L + A^*$, where

$$A^* = (\sigma_K/\overline{K})^2 x \qquad (2.7)$$

and x is the distance traveled ($x = vt$). The value of dispersivity given in Eq. (2.7) is equal to the value of dispersivity implied in an analysis of dispersion by Mercado (1967), where

$$\sigma_x = (v\sigma_K/K)t \qquad (2.8)$$

and then

$$A^* = (d\sigma_x^2/dt)/2v, \qquad (2.9)$$

from which Eq. (2.7) follows. Here, σ_K is the standard deviation of the hydraulic conductivity distribution and σ_x is the standard deviation of the concentration distribution.

According to Eq. (2.7), dispersivity should increase linearly with distance traveled. According to Mercado's result [Eq. (2.8)], the standard deviation of the concentration distribution increases linearly with time or distance. If dispersion is Fickian, the standard deviation increases with the square root of the distance traveled. Thus, the dispersed zone grows more rapidly before the Taylor limit is reached.

Pickens and Grisak (1981a) suggest using Eq. (2.7) or some similar equation in the standard advection-dispersion equation to describe the early portion of the dispersion process. Matheron and DeMarsily (1980) consider a similar approach based on the concept of an equivalent dispersivity:

$$\alpha_{L_i} = \sigma_{xi}^2/2vt, \qquad (2.10)$$

where σ_{xi}^2 is the variance of the concentration distribution at time i. Eq. (2.10) follows directly from Eq. (2.9) for a discrete time interval. The values of longitudinal dispersivity (α_{L_i}) are defined such that α_{L_i} represents dispersion for the time from

$t = 0$ to $t = t_1$ and α_{L_1} represents dispersion for the time from $t = t_1$ to $t = t_2$, for example. However, Matheron and DeMarsily (1980) caution that because the use of Eq. (2.10) implies that dispersivity is really a constant and because the advection-dispersion equation is actually inapplicable for early times, the use of an equivalent dispersivity is not completely satisfactory. They conclude that, "A better mathematical formulation of the transport process in porous and fractured media, valid for all time, seems necessary." More specifically, according to Gillham and Cherry (1982): "The present challenge is to develop a physically based transport model that incorporates spatially and/or temporally variable dispersion parameters that can be determined in a practical manner and with an acceptable degree of certainty."

SUMMARY AND DISCUSSION

The discussions of dispersion in the preceding sections focused on applications to continuous porous media; dispersion in fractured porous media will be considered in a later section of this chapter. The state of the art for quantifying dispersion in continuous porous media is summarized below.

Results from several studies suggest that dispersion is non-Fickian near the source of the contaminant and therefore the standard form of the advection-dispersion equation does not apply. A modified form could be derived for analyzing non-Fickian transport for small times. Gelhar et al. (1979) presented such an equation for one-dimensional flow in a perfectly stratified aquifer. However, they caution that the approach that they used to derive the equation requires certain restrictions that may not be valid at small times. Other approaches that rely on the standard form of the advection-dispersion equation call for use of time-dependent dispersivities (Gill and Sankarasubramanian, 1972; Matheron and DeMarsily, 1980; Pickens and Grisak, 1981b).

The standard approach in analyzing dispersion involves the use of an average linear velocity [Eq. (2.1)] and the use of a dispersion term [Eqs. (2.2) and (2.3)] to represent deviations of velocity from the average. The rationale for this approach is based on the premise that a dispersion term is necessary because it will never be practical to define the velocity field in detail. Moreover, according to Dagan (1982) it is inappropriate to assume that local dispersion does not influence advection. Hence, several investigators (Gelhar et al., 1979; Gelhar and Axness 1981, Dagan, 1982) maintain that the key to a rational application of the advection-dispersion equation is to define the dispersivity in terms of various statistical properties of hydraulic conductivity.

Another approach, used by Schwartz (1977) and Smith and Schwartz (1980, 1981a, 1981b) among others, is based on attempts to represent the velocity field in detail by defining the hydraulic conductivity in a stochastic manner and in this way to simulate the effects of macroscopic dispersion directly. Smith and Schwartz (1980) concluded that for their simulations local dispersion was negligible because most dispersion observed in their modeled systems occurred at a macroscopic scale. Therefore, in subsequent studies (Smith and Schwartz, 1981a, 1981b)

they used an advective model to simulate contaminant transport in a number of hypothetical systems characterized by different arrangements and shapes of heterogeneities. Results of their numerical experiments demonstrated that the solution of the contaminant transport model is quite sensitive to the structure of the heterogeneities within the porous material. Consequently, detailed information on the arrangement and shapes of the heterogeneities, knowledge of the values of hydraulic conductivity for the various units, and information on head gradients (or direct measurements of velocities) are essential for accurate prediction. Although they demonstrated that it is theoretically possible to predict contaminant transport given sufficient hydrogeologic data, they remained pessimistic regarding the practical limitations of obtaining the detailed information needed (Smith and Schwartz, 1981b). In addition they concluded that ". . . large uncertainties can be associated with transport predictions in heterogeneous media. These uncertainties must be dealt with in order to develop confidence in the application of mathematical models of site-specific problems. Unfortunately, the variety of possible sources of uncertainty and the difficulty in controlling their size suggest that progress will be slow." Similarly, Dagan (1982) concluded that "longitudinal dispersion can be represented asymptotically by a Fickian equation, with dispersivity much larger than pore-scale dispersivity," but given the uncertainties involved in defining the hydrogeologic system a stochastic approach is necessary and "the traditional approach of predicting solute concentrations by solving deterministic partial differential equations is highly questionable in the case of heterogeneous formations."

The conclusion drawn from these studies is that although there has been considerable progress within the past 5 years in understanding the nature of macroscopic dispersion in porous media, to date, a credible, practical, and reliable model for analyzing contaminant transport near the source has not been identified. However, theoretical studies by several researchers suggest that for large times (or large travel distances) the dispersion component of the advection-dispersion equation can be represented by an expression analogous to Fick's second law of diffusion [Eq. (2.2)], and therefore the classical advection-dispersion equation will accurately simulate contaminant transport in porous media, provided that dispersivity can be quantified in a meaningful way.

Gelhar et al. (1979), Gelhar and Axness (1981), and Dagan (1982) present formulas for defining dispersivity at large times in terms of statistical parameters. However, several investigators suggest that the length of time that must elapse before the advection-dispersion equation is applicable may be appreciable. Specifically, the travel distance of the contaminant must be on the order of 10s or 100s of meters from the source before the advection-dispersion equation is valid. Simulations of contaminant transport by Pickens and Grisak (1981b) suggest that the scale dependence of dispersivity at early times may have little effect on results for large times or travel distances. Hence, the use of an asymptotic dispersivity may be adequate for these conditions provided that sufficient geologic data are available to characterize the statistical parameters of the hydraulic conductivity distribution (the variance and the correlation scales), as well as the orientation of the geologic units. More attention

is needed in characterizing geologic systems in terms of these statistical parameters (e.g., see Smith, 1981; Neuman, 1982). Moreover, field data needed to corroborate the theory itself are lacking. There is also a need for carefully designed field tracer tests to determine whether the theory is generally applicable and to serve as a basis for estimating the length of time before the Taylor limit is reached and Eq. (2.4) is valid. Data from such tracer tests would allow an assessment of the reliability of recently derived expressions for dispersivity.

DISPERSION IN FRACTURED ROCK

The discussion in previous sections focused on dispersion in continuous porous media. Application of dispersion analysis to contaminant transport in fractured rock is in its infancy, yet it is of considerable importance. Certain types of fractured rock, such as shale, granite, and salt, are likely candidates for repositories of high-level nuclear waste, and clay, which is also susceptible to fracturing, is currently used as a disposal medium for municipal, industrial, and low-level radioactive wastes.

Recent work on flow through fractured rock has emphasized laboratory investigations and development and testing of mathematical models, most of which are based on the concept of a dual porosity medium (e.g., Grisak and Pickens, 1980; Neretnieks, 1980) as shown in Figure 2.5. In a few cases, models have been used in conjunction with results from laboratory experiments (Grisak et al., 1980; Tang et al., 1981; Neretnieks et al., 1982) and field data (Bibby, 1981). These results support the following conclusions:

1. Diffusion of contaminants from fractures to the rock matrix can serve as a significant retardation mechanism (see Grisak and Pickens, 1980; Neretnieks, 1980; Abelin et al., 1982; Birgersson and Neretnieks, 1982). This phenomenon is illustrated schematically in Figure 2.5.

2. Dispersion in the fracture can significantly accelerate the arrival of contaminants at a discharge point when velocities in the fractures are relatively low.

Experimental results suggest that velocity in fractures can be represented using the so-called cubic law (see Witherspoon
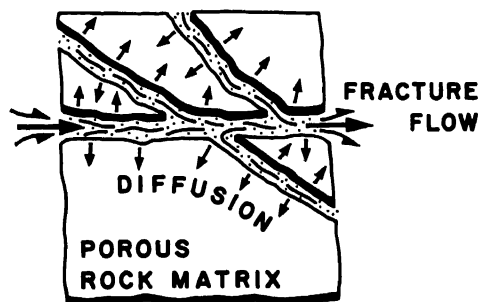

FIGURE 2.5 Schematic diagram representing flow through fractures and diffusion of contaminants from fractures into the rock matrix of a dual porosity medium.

et al., 1980), which is a form of Darcy's law in which the equivalent hydraulic conductivity of the fracture (K_f) is

$$K_f = (\rho g/12\mu)b^2, \qquad (2.11)$$

where b is the aperture of the fracture, g is the constant of acceleration of gravity, ρ is the density of water, and μ is the dynamic viscosity. The cubic law for the volumetric flow rate through the fracture is

$$Q = (\rho g/12\mu)IWb^3, \qquad (2.12)$$

where I is the head gradient across the length of the fracture segment and W is the width of the fracture segment.

A number of models (Grisak and Pickens, 1980; Tang *et al.*, 1981; Neretnieks *et al.*, 1982) consider dispersion in the fracture. Tang *et al.* (1981) derived an analytical solution of the advection-dispersion equation for one-dimensional contaminant transport with longitudinal dispersion in the fracture, coupled to a solution of a model representing diffusion of solute from the fracture into the rock matrix. Grisak and Pickens (1980) solved a similar problem using a finite-element model. Both concluded that while longitudinal dispersion in the fracture can be important, little is known regarding the magnitude of dispersivity in fractures except that it is a function of the roughness of the fracture. Experiments under way (see Witherspoon, 1981) may help in quantifying fracture roughness, which is a first step toward quantifying dispersivity in fractures.

Analysis of flow of water through networks of fractures has been attempted (Bibby, 1981; Neuzil and Tracy, 1981; Sudicky and Frind, 1982). But much additional work is needed to test and to modify these types of models. A major impediment to testing of fracture flow models is the difficulty of obtaining field data that describe the hydrogeologic characteristics of fractured rock.

CONCLUSIONS

1. There has been significant progress in quantifying dispersion in porous material since 1978.

2. The consensus is that dispersion in porous material is non-Fickian near the source of the contaminant, and therefore for small times or small distances from the source, the standard form of the advection-dispersion equation does not apply.

3. There is no consensus regarding the best way to quantify dispersion near the source of the contaminant. Some researchers prefer to aim at attempting to describe the velocity field in sufficient detail so that contaminant transport can be simulated by advection alone. Others prefer to rely on refining the advection-dispersion equation to handle non-Fickian dispersion.

4. Theoretical studies suggest that for many hydrogeologic settings, dispersion should become Fickian for large times or large distances (on the order of 10s to 100s of meters). In this case it is possible to express the dispersion parameter known as dispersivity in terms of statistical properties of the hydraulic conductivity distribution.

5. Carefully designed field tracer tests are needed to eval-

uate the applicability of the theory for large times and to refine the theory for small times.

6. Detailed hydrogeologic information is needed to predict dispersion for both small and large times.

7. The concept of a dual porosity media (Figure 2.5) is currently used for modeling groundwater and contaminant flow through fractured rock. However, the difficulties involved in characterizing the geometry of a fractured-rock system in the field complicates the testing of the theory. As a result, none of the models developed to simulate dispersion and diffusion of contaminants in fractured rock have been verified by field experiment.

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Contaminants in Groundwater: Chemical Processes

3

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ABSTRACT

The movement of most toxic contaminants in groundwater is affected by chemical reactions that cause transfer of contaminant mass between the liquid and solid phases or conversion of dissolved species from one form to another. The chemical attenuation of inorganic contaminants occurs mainly by adsorption, precipitation, oxidation, or reduction. Organic contaminants can be adsorbed or degraded by microbiological processes, but at present little is known about their behavior, particularly under the anaerobic conditions that are common in contaminated groundwater.

Field and laboratory studies have established that various toxic heavy metals, transition metals, metalloids, radionuclides, and other inorganic species can be mobile or immobile in the groundwater zone, depending on the hydrogeochemical conditions represented by the pH, the redox condition, the ionic strength, the mineralogy, the solid-phase surface area, and the complexing capacity. Although the importance of chemical reactions in the attenuation of contaminants is widely recognized, the capabilities for attenuation predictions are not well developed. This is the case because the chemical processes within dynamic groundwater systems are complex; consequently, many of the geochemical parameters in predictive models are problematic. The prediction problem is complicated by the fact that the chemical processes are continually influenced by the redistribution of dissolved species caused by molecular diffusion and mechanical dispersion. The complexities of these mixing processes contribute to the difficulties in developing reliable methods for predicting the chemical behavior of contaminants in the groundwater zone.

INTRODUCTION

Contaminants can enter the groundwater zone from regional sources such as agricultural fields on which fertilizer or pesticides have been applied or from local sources such as landfills or waste spills. Within the groundwater zone, migration of the contaminants is influenced by advection, mechanical dispersion, molecular diffusion, and chemical mass transfer. To predict the behavior of contaminants in groundwater the effects of each of these influences must be adequately represented in a model or group of models. This chapter focuses on the processes that cause chemical mass transfer and on the manner in which these processes are represented in models. Emphasis is

placed on inorganic contaminants and, in particular, on those elements or compounds that have concentration limits specified in drinking-water standards. These include various transition metals, heavy metals, metalloids, and nonmetallic constituents such as nitrate. Nearly all of the literature describing the chemical behavior of contaminants in groundwater pertains to these inorganic constituents.

The number and quantity of organic chemicals that are produced have increased continuously since World War II. More than 3,000,000 organic compounds are known to exist and more than 40,000 are currently manufactured. Many of these are hazardous or potentially hazardous. In recent years many common organic chemicals have been recognized to be hazardous

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and relatively mobile in permeable groundwater systems. In some regions widespread contamination by organic compounds exists in shallow groundwater. Organic compounds in groundwater can also cause major changes in the chemical behavior of inorganic constituents because of inorganic-organic reactions. Because there is a paucity of information on the behavior of dissolved organic compounds in groundwater, only a brief review of this subject is presented here. The emphasis in this chapter is on the chemical behavior of dissolved contaminants in porous geologic deposits. Only minor consideration is given to contaminant behavior in fractured rock or in fractured nonindurated materials. The movement of immiscible organic liquids in subsurface systems is not considered in this chapter.

TRANSPORT WITH CHEMICAL MASS TRANSFER

A common problem in the evaluation of the existing and future quality of groundwater is the determination or prediction of the effect of local sources of contamination. Examples of local sources are municipal and industrial landfills, industrial lagoons, roadsalt storage piles, septic sewage systems, mine and mill wastes, livestock feedlots, and local spills of industrial or agricultural chemicals. When local degradation of groundwater quality occurs, it is usually the result of downward movement into the groundwater zone of leachate from wastes or of spilled chemicals or waste liquids. As the contaminant solution migrates through the groundwater system, it displaces the original groundwater. The chemical composition of the zone of contamination continually changes because of dispersion, diffusion, and chemical reactions. The chemical reactions are driven by the changes in the chemical conditions caused by dispersion and diffusion and by the contact of the contaminated water with the surfaces of minerals and amorphous solids in the medium. Chemical changes in the zone of contamination may also be fostered by bacteria in the groundwater system.

There are two main approaches that are commonly used for the prediction of the behavior of most chemically reactive inorganic contaminants in groundwater. The first approach involves the incorporation of a simple chemical mass-transfer term representing adsorption in the advection-dispersion equation. This approach has the objective of predicting the advance rate and the shape of the front of a contaminant zone emanating from a continuous or a temporary source. The second approach has the objective of predicting the contaminant concentrations that will occur in the zone of contamination after chemical mass transfer has caused equilibrium concentrations to be achieved by precipitation, dissolution, oxidation, or reduction. The first approach has its origins in applied chemical chromatography, and the second was adapted from the chemistry of electrolyte solutions by geochemists interested primarily in seawater and surface continental waters. The processes of adsorption, dissolution, precipitation, oxidation, and reduction usually occur simultaneously in zones of contaminated groundwater; therefore, the use of predictive methods that represent adsorption with exclusion of the effects of the other processes or the other processes with the exclusion of adsorption is usually based on

convenience of conceptualization and computation rather than a quest for realism.

Adsorption in Advective-Dispersive Systems

Most currently used models for the prediction of transport of nonreactive dissolved contaminants in the groundwater zone are based on the advection-dispersion equation. The development of this equation is described by Anderson (Chapter 2 of this volume). Adsorption is usually incorporated into this equation in a manner based on the assumption that the concentration of the contaminant in the solution phase (C) is a function of the concentration in solid phase $(\overline{C})$, or

$$C = f\overline{C}. \tag{3.1}$$

With this assumption, the advection-dispersion equation for homogeneous saturated porous media is

$$\partial C/\partial t = D\partial^2 C/\partial x^2 - V\partial C/\partial x - [(\rho/n)K_s]\partial C/\partial t, \tag{3.2a}$$

where x is the flow direction, D is the dispersion coefficient in the direction of flow, V is the average linear groundwater velocity, ρ is the dry bulk density of the porous medium, n is the porosity, t is time, and K_s is the slope of the functional relationship expressed in Eq. (3.1). The last term on the right-hand side of Eq. (3.2) represents the contaminant mass that is lost from solution as a result of adsorption. When the K_s function is known, mathematical solutions for Eq. (3.2a) or for its two- or three-dimensional forms (including representation for heterogeneous geologic systems) can be obtained by means of numerical methods. It is important to recognize that Eq. (3.1) is based on the assumption that equilibrium conditions exist between the solution-phase and solid-phase concentrations. Theoretically, Eq. (3.2a) is only applicable if the reactions are instantaneous or, in practice, only if the reactions are fast relative to the groundwater velocity.

In some situations, the relation between C and $\overline{C}$ is linear, and thus the slope of the partitioning function (K_s) becomes a constant and is generally referred to as the distribution coefficient (K_d). In this situation Eq. (3.2a) can be expressed as

$$\partial C/\partial t = D'\partial^2 C/\partial x^2 - V'\partial C/\partial x, \tag{3.2b}$$

where D' is the effective dispersion coefficient $(D' = D/R)$ and V' is the rate of advance of the front of the contaminant zone $(V' = V/R)$ in the absence of dispersion. This front is retarded relative to the rate of advection of the front of nonreactive contaminants (V). R is the retardation factor, defined as V/V' and is represented by the retardation equation,

$$V/V' = 1 + (\rho/n)K_d. \tag{3.3}$$

In the absence of dispersion the front is conceptualized as a plug-displacement front. In the presence of Gaussian dispersion, it represents the 50th percentile concentration level of an advancing slug of contamination (i.e., the middle of the dispersed front) emanating from a continuous source. The retardation concept is illustrated schematically in Figure 3.1 for laboratory conditions and for a hypothetical field situation. For the field example, the groundwater velocity is assumed to have little spatial or temporal variability.

LABORATORY REPRESENTATION
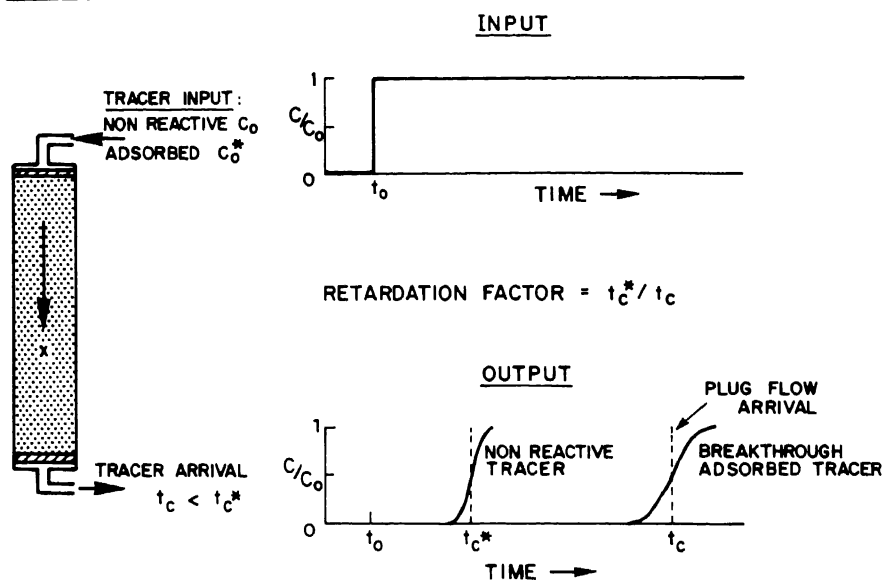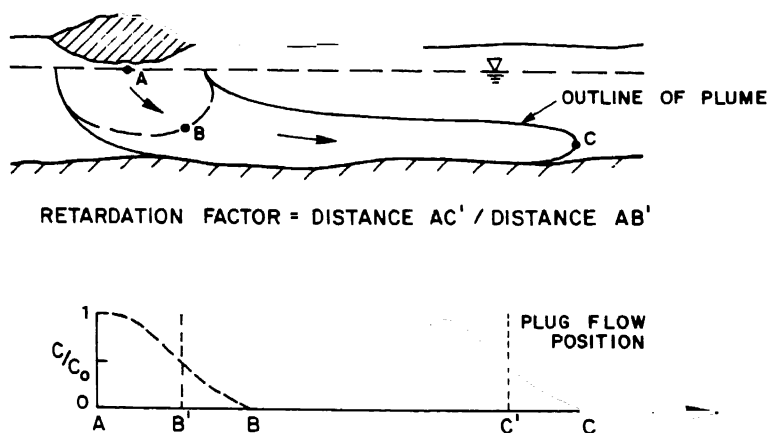
FIGURE 3.1 Schematic illustration of the retardation concept: the ideal laboratory case and a hypothetical field case.

When K_d represents the partitioning relation in Eq. (3.3), the many available analytical and numerical mathematical solutions (e.g., Bear, 1972; Fried, 1975; Pinder and Gray, 1977) for the advection-dispersion equation for nonreactive contaminants in saturated homogeneous porous media can be used for predictive purposes. In these models the velocity of the advancing front becomes the effective contaminant velocity, V/R, and the dispersion coefficient becomes the effective dispersion coefficient, D/R.

The retardation relation and the use of the distribution coefficient in the advection-dispersion equation were introduced by Higgins (1959) into the literature on contaminant migration in groundwater. The use of the distribution coefficient in studies pertaining to the disposal of radioactive waste became common in the 1960s and 1970s. More recently this approach has been used in studies of the behavior in groundwater of various adsorbed nonradioactive elements, such as transition metals,

heavy metals, metalloids, and trace organic compounds. Although the convenience of the approach is beyond dispute, its validity as a means of developing reliable predictions of the behavior of inorganic contaminants in actual groundwater systems is questionable in many situations.

The $C = f\bar{C}$ relation is normally determined in the laboratory by means of batch tests in which a known mass of the geologic medium (in particulate form) is immersed in a solution representing the leachate or groundwater. The solution contains a specified concentration of the contaminant of interest. After agitation of the liquid-solid mixture for a period of hours or days, the contaminant concentration in solution is determined and, by difference, the concentration adsorbed on the solids is known. When this test is repeated using different concentrations of the contaminant in solution, the $C = f\bar{C}$ relation, which is known as the adsorption isotherm, is obtained.

There are many possible functional forms of adsorption iso-

therms, a large number of which are described by Smith (1970). However, in studies of trace-level contaminants in geologic media, isotherms from batch tests usually fit closely to a functional relation known as the Freundlich isotherm,

$$C = k\bar{C}^a, \qquad (3.4)$$

where k and a are empirical coefficients. If $a = 1$, the isotherm is linear, then $k = K_d$, and Eq. (3.3) is applicable. If $a > 1$, the concentration versus distance profile in the flow direction is narrow and the contaminant mass in solution advances less rapidly than would be the case for linear adsorption. If $a < 1$, the concentration profile is broad and the contaminant mass in solution advances more rapidly than in the linear case.

Much of the earlier literature on distribution coefficients and the retardation equation pertains to cationic radionuclides, such as radioisotopes of Sr and Cs, present in very low concentrations. The isotherms for these isotopes at low concentrations are nearly always linear. In recent years batch isotherms have been determined for various nonradioactive elements such as Ag, As, Cd, Cr, Pb, and Se. When present at trace concentrations under conditions where adsorption rather than precipitation is the controlling mass-transfer process, these elements commonly yield isotherms that in some cases are nonlinear but that can be described by the Freundlich relation. Davidson *et al.* (1976) presented the results of numerical advection-dispersion-based simulations of the movement of slugs of contaminants with different Freundlich isotherms having various values of a. They concluded that serious errors in predictions of migration may occur when a linear isotherm is assumed for contaminants that exist at high concentration.

Limitations of the Adsorption-Isotherm Approach

Limitations and uncertainties are inherent in the use of the isotherm approach within the framework of the advection-dispersion equation. The uncertainties exist because of the heterogeneous nature of geologic deposits, because of geochemical effects, and because of effects caused by the dynamics of the transport process.

The primary mechanism of adsorption is commonly ion exchange, which, for univalent species, can be represented as

$$X^+ + AS = A^+ + XS, \qquad (3.5)$$

where X^+ is the cationic contaminant in solution, XS is the contaminant in the adsorbed states on the exchange medium designated as S, and A^+ is the resident cation initially on the exchange medium. Application of the law of mass action provides

$$K_{ex} = [A^+][XS]/[X^+][AS], \qquad (3.6)$$

where K_{ex} is the equilibrium coefficient for the exchange reaction and the bracketed terms are thermodynamic concentrations or activities. Conversions between activities and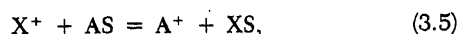 concentrations for dissolved species can be made using activity coefficients as described below. For situations when the contaminant of interest is present in very small concentrations relative to the concentration of the exchangeable cation in the medium and when the exchange between the contaminant (X^+)

and the exchangeable cation (A^+) does not cause a significant change in the activity ratio $[A^+]/[AS]$ (designated as r), it is apparent that K_d is a constant, and

$$K_d = K_{ex}/r = (XS)/(X^+), \qquad (3.7)$$

where the quantities in parentheses are concentrations. The activity coefficients are neglected.

This development of the distribution coefficient provides a convenient basis for identification of one of the major difficulties in the distribution-coefficient approach. Consider a situation where a leachate or spilled liquid enters a groundwater-flow system. The leachate contains contaminant X^+, which exists in a zone that is retarded relative to the movement of the rest of the leachate zone. In addition, this zone contains a variety of dissolved constituents including the competitor cation A^+, which exists in the leachate at concentrations different than the ambient groundwater. Therefore, each segment of the porous medium contacted by X^+ has been contacted previously by the major cations (including A^+) in the leachate that travels in advance of the retarded zone that contains X^+. Because of this contact, the occupancy of the exchange sites evolves toward a new steady-state condition that is not represented in the normal batch tests used to determine the distribution coefficient. It is common practice in batch tests to use water that has major-ion concentrations made up to represent the ambient groundwater from the field site, or in some cases field samples of ambient groundwater are used. Even if the aqueous solution used in the determination of the distribution coefficient by the batch method has the same composition as the leachate, the condition in the field is different because the advancing zone of contamination continuously supplies cations to the exchange sites. In the normal type of batch test the solids are immersed in the test solution only once. Using exchange theory and a mixing-cell model, Reardon (1981) demonstrated that exchange involving major cations, such as Ca^{2+} and Na^+, can cause a gradual change in the ratio r as the zone of contamination continuously passes through the porous medium. As can be deduced from Eq. (3.7), this causes a progressive change in the K_d for X^+ in an advancing zone of X^+ contamination. In recognition of this difficulty, however, batch tests can be conducted in a manner that more closely represents field conditions. In some cases additional laboratory tests combined with the use of models such as the one described by Reardon can be used to show that the magnitude of change in r is insignificant relative to the accuracy required of the K_d values for the particular predictive task.

In some situations, the contact between the porous medium and the less retarded contaminants can cause alteration of the exchange properties of the porous medium as a result of precipitation, dissolution, oxidation, or reduction. For the movement of a species controlled by adsorption to be simulated in a realistic manner, it would be necessary to simulate the changes in exchange properties that occur because of all geochemical influences. This is currently beyond the scope of existing models, except for the simplest cases involving exchange of major cations or of trace constituents with exchange properties known for specified or measurable conditions of pH and major dissolved constituents.

Transport models that represent the exchange of major cations and that are based directly on the law of mass action were described by Valocchi et al. (1981), who incorporated exchange theory into a numerical advection-dispersion model, and by Dance and Reardon (1982), who used mixing-cell models, and Schultz and Reardon (1983). These models have been used successfully in the simulation of the transport of major cations in aquifers into which wastewater or tracer solutions were injected.

The use of the isotherm approach rests on the premise that isotherms can be determined in the laboratory on samples that are representative of the geologic materials as they exist in the field. It is generally not feasible to collect samples of geologic materials and transfer them to the laboratory without, in some manner, altering their geochemical characteristics. Some of the more obvious processes that are difficult to control or exclude during field sampling and during batch testing include the invasion of oxygen and the degassing of CO_2. These processes can alter the redox condition and pH of the samples, with the potential to cause significant changes in the concentrations of the competing cations and to cause alterations in the exchange characteristics of the solid phase. Oxygen invasion and sample drying can cause precipitation of iron and manganese hydroxides, which have a strong affinity for adsorption of cationic and anionic trace contaminants. Studies of batch tests (Hajek and Ames, 1968; Routson and Serne, 1972) have shown that the measured K_d can also be influenced by experimental factors such as the ratio of solution to solids used in the tests. Ralyea et al. (1980) recommended procedures for determining K_d values of radionuclides by batch tests. Although these procedures would tend to minimize the influence of the foregoing effects, the effects cannot be entirely eliminated and will generally contribute to the uncertainty in the predictions generated by models in which K_d values are used.

The second inherent type of uncertainty in the isotherm approach to advection-dispersion modeling pertains to the dynamic conditions that occur in the porous medium during trans-port. Breakthrough curves that are simulated using the advection-dispersion model with linear isotherms are symmetrical or nearly symmetrical, whereas curves obtained from laboratory-column experiments are asymmetrical with extended tails. Reynolds (1978) compiled data from several published studies in which tracers with linear batch isotherms were used to obtain breakthrough curves from column experiments. The results were scaled and plotted on the same graph of dimensionless concentration versus dimensionless time (Figure 3.2). The data for Figure 3.2 represent the work of several investigators and a variety of sorbates and sorbents. All the breakthrough curves are asymmetrical and fit within a single narrow band on the dimensionless graph. This suggests the presence of a common factor that is currently not accounted for in the advection-dispersion formulation.

One proposed explanation for the asymmetry of the breakthrough curves invokes the presence of physical or chemical kinetic effects. For example, Cameron and Klute (1977) and others simulated curves of the type shown in Figure 3.2 by the addition of an empirically derived first-order kinetic term to Eq. (3.2). Van Genuchten et al. (1974) developed an equation having a similar form but attributed the kinetic parameters to the rate-dependent migration of the solute into zones of immobile water. Reynolds et al. (1982) obtained breakthrough curves for Sr^{2+} that exhibited the typical asymmetrical form with extended tails even though the velocities used in the tests ranged over an order of magnitude. This apparent velocity independence of the shape of the breakthrough curves casts doubt on the kinetic explanation of the observed tailing.

James and Rubin (1978) showed that the transport equation with a linear-adsorption term accurately predicted the migration of cations when the flow velocity was so slow that molecular diffusion was the dominant influence in the dispersion process. At higher velocities when mechanical mixing was dominant in the dispersion process, the differences between measured and calculated breakthrough curves were similar to that represented in Figure 3.2. The results of James and Rubin at very
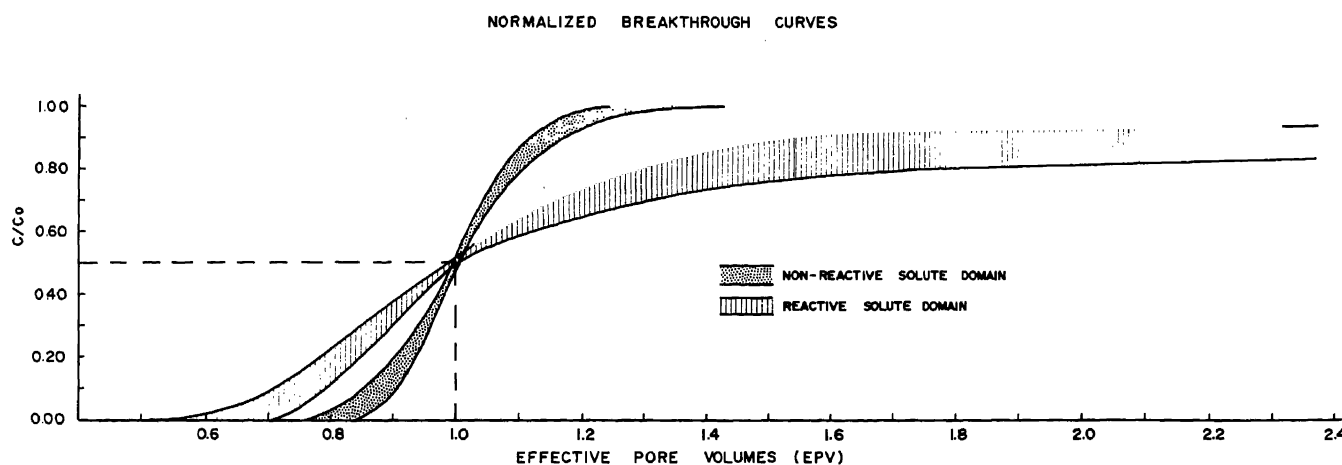

FIGURE 3.2 Breakthrough graphs for nonreactive and adsorbed tracers in column experiments with homogeneous porous media. Each graph represents numerous sets of experimental data from Gillham and Cherry (1982).

low velocity are consistent with unpublished diffusion data obtained at the University of Waterloo, using the same materials as those used by Reynolds *et al.* (1982). The evidence suggests that the discrepancy between measured and predicted curves is, in some way, the result of the advection process; however, the manner by which advection causes the discrepancy is not known. The measured curves can be closely matched with simulated curves when a kinetic term is included in advection-dispersion models, but at present the kinetic parameters are determined arbitrarily by curve fitting. An understanding of the processes may lead to a less arbitrary means of specifying values for the parameters, thus improving the predictive reliability of the models.

The asymmetrical shape and tailing of breakthrough curves for adsorbed contaminants have considerable practical importance for predictions of the first arrivals of contaminants and for predictions of the rates and effectiveness of purging of zones of contamination from aquifers by means of pumping-well systems. For contaminants that are hazardous at very low concentration levels, prediction of the behavior of the front or tail of a contaminant zone (where the contaminant occurs only at extremely low concentration levels) can be more important than predictions of the arrival of the center of mass or mid-level concentrations that are represented by the retardation equation [Eq. (3.3)]. The fact that laboratory studies provide evidence of a lack of predictive capability for behavior of fronts and tails does not bode well for prediction under field conditions.

Some of the uncertainties that are inherent in the use of laboratory-determined distribution coefficients in advection-dispersion models can be avoided if the effects of adsorption are assessed by field tests using tracers that adsorb and others that do not react with the porous medium. Values for the retardation factor (R) are computed from the differences in rates of passage through the test zone in the aquifer. Goodwin and Gillham (1982) conducted miniature field tracer tests to obtain radionuclide retardation factors using a device attached to the head of hollow-stem augers used in boreholes in sand deposits. A more common type of test involves the injection of hundreds or thousands of liters of tracer solution into aquifers. An example of a field test of this type is described by Ewing (1959). These tests are relatively expensive, and, in order to obtain results in a practical length of time, they are generally only suitable for application in zones that have moderate or high hydraulic conductivity and low retardation factors. Although values for the retardation factor can be estimated from field-tracer tests, the suitability of these values for use in predictions that pertain to spatial or temporal scales much different than those represented by the tracer test is problematic. When advection-dispersion models are used in the analysis of the tracer-test data, apparent nonlinear behavior may necessitate the use of a separate kinetic adsorption term as a means of obtaining a close match between simulations and the test data or the use of nonequilibrium physical/chemical or adsorption parameters within the dispersion term. An example of the latter approach in a field tracer investigation is provided by Pickens *et al.* (1981). Whether these approaches provide a reliable basis for prediction remains to be established.

Not many detailed comparisons between migrations of adsorbed inorganic contaminants observed in the field and predicted migrations based on laboratory batch tests exist in the literature. The few that we are aware of involve cationic radionuclides in groundwater. These comparisons show moderately good agreement between observed retardation and simulated retardation based on data from laboratory tests (Ewing, 1959; Jackson and Inch, 1980; Gomer, 1981). In some situations order-of-magnitude estimates of contaminant retardation are all that is required for solution of a practical problem, in which case many of the sources of uncertainty in the predictive approach may be unimportant.

Precipitation and Solubility Controls

The behavior of many deleterious or toxic inorganic contaminants in groundwater is influenced by chemical precipitation that occurs as the contaminant adjusts to solubility constraints. The prediction of solubility constraints is based on the law of mass action and the associated principles of equilibrium-chemical thermodynamics. The objective is to predict the equilibrium concentration of the contaminant species of interest under the conditions that exist or will exist in the groundwater zone. In the conceptualization of the predictive task, the leachate or waste solution in some initial state enters the groundwater system and adjusts by means of various reactions to an equilibrium state within the groundwater system.

Equilibrium is achieved as a result of one or more of the following processes: precipitation, dissolution, oxidation, reduction, hydrolysis, or complexation. This approach is similar to that described above for contaminants that are adsorbed in that both approaches are based on the assumption of equilibrium; however, the two approaches are very different. The first describes the advance of the front of the contaminant zone as chemical mass transfer continuously occurs in response to a changing solution-phase concentration, whereas the second describes the equilibrium concentrations that occur after chemical mass transfer in a reaction zone has caused equilibrium to be achieved. According to this conceptualization, chemical mass transfer occurs in the reaction zone, and in front of the reaction zone the contaminants are transported at the equilibrium concentrations established previously in the reaction zone. This is the case if the chemical nature of the porous medium does not change along the flow path. Although it may be possible to specify the rate of entry of the contaminant solution into the groundwater system, the chemical-equilibrium approach provides no information on the rate of advance of the reaction zone because reaction rates and the availability of reactants are not included in the description of the system. Even if kinetic terms were included in the computational routines, so little is known about the reaction-rate controls in contaminated-groundwater systems that little additional predictive capability would be gained. The computational routines for representation of complex equilibrium hydrogeochemical systems have not yet been incorporated in a practical manner in advection-dispersion models. Excessive cost of computer time is currently one of the major limiting factors in the development of this approach as a practical means of prediction.

The equilibrium relation for a contaminant species controlled

by precipitation or dissolution is specified as

$$xX + bB = yY + cC + dD, \qquad (3.8)$$
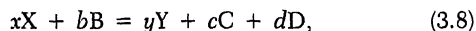
where X is the inorganic contaminant species in the solution phase; Y is a mineral or solid amorphous compound in which the contaminant species is incorporated by precipitation or from which it is released by dissolution; B, C, and D are other elements or compounds in solution; and x, y, b, c, and d are the stoichiometric mole numbers. From the law of mass action, the equilibrium expression is obtained:

$$X = [C] \cdot [D]/K_{eq}[B], \qquad (3.9)$$

where K_{eq} is the equilibrium constant and the quantities within the brackets are chemical activities, which can be converted to concentration using well-established conversion relations (Stumm and Morgan, 1980). If X (in the leachate or spilled liquid) is initially above the equilibrium concentration when it enters the groundwater system, adjustment toward equilibrium will occur by precipitation of mineral or amorphous solids. If X is below the equilibrium concentration, minerals or amorphous solids that contain X as part of the chemical structure will dissolve when such solids are present in the system. If they are not present, which is usually the case for most contaminants of interest, the condition of undersaturation will persist.

For example, if Pb is the contaminant of interest, and if $PbCO_3$ is the solid phase that may control the solubility of Pb, the equilibrium expression would be

$$K_{eq} = [Pb^{2+}][CO_3^{2-}], \qquad (3.10)$$

where $[CO_3^{2-}]$ would depend on the pH and the dissolved inorganic carbon. The total concentration of dissolved Pb would be represented by the sum of the concentrations of Pb^{2+} and the other species of Pb in solution, which would include complexes and hydrolyzed species (see next section). To determine which solid phase would be expected to exert the major solubility control, equilibrium relations for many compounds of Pb would be considered.

For reactions involving nearly all minerals or amorphous inorganic compounds of interest, values for the equilibrium constant at 25°C can be obtained from published listings, or they can be computed from values of the standard free energies of reaction in published compilations of thermodynamic data.

When a contaminant in a leachate or waste liquid enters the subsurface domain, the chemical reactions cause adjustment of the solution to the new conditions. The reactions are influenced by the minerals that comprise the porous medium, by the degree of mixing that occurs between the contaminant solution and the ambient groundwater, by changes in temperature and pressure, and, in some cases, by microbial action. To predict the equilibrium concentration of a particular trace contaminant by means of Eq. (3.9), it is first necessary to predict the gross chemical composition of the contaminant solution after the dominant reactions in the subsurface domain have proceeded to equilibrium or to some other expected status. The gross chemical composition is represented primarily by the major ions such as Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, and dissolved inorganic carbon. In many cases K^+, Fe^{2+}, H_2S, NH_4^+, or NO_3^- also occur as important components of the gross chemical composition of the water. The reactions that involve the above constituents normally determine the ionic strength, pH, and redox status of the groundwater. These parameters have an important influence on the solubility of most toxic inorganic contaminants, which usually constitute only a small percentage of the total dissolved solids. In practice, the use of Eq. (3.9) is the last stage in a series of predictions involving numerous chemical reactions with various assumptions regarding the choice and status of the reactions. So little is known about the identities and quantities of reactive minerals in many groundwater systems that considerable speculation is often used in the representation of the suite of reactions that control the gross water chemistry.

Computer codes, such as the one described by Parkhurst et al. (1980), are available for performing the computational tasks in predictions of the gross equilibrium chemistry of groundwater that reacts with various minerals and amorphous solids. The available equilibrium constants and free energy data are generally for 25°C. Extrapolations to the lower temperatures common for most contaminated groundwater are generally accomplished without large uncertainties. Nearly all of the thermodynamic data for solid phases is derived for chemically pure manifestations of the minerals, whereas in groundwater impurities are the norm. When solids precipitate in the groundwater zone, amorphous or poorly crystalline forms commonly exist at first and then slowly undergo conversion to more crystalline forms. The thermodynamic properties for the less crystalline forms are not well known. Some reactions for precipitation, dissolution, oxidation, or reduction do not proceed quickly to equilibrium. These deficiencies notwithstanding, the chemical equilibrium approach for prediction of the concentrations of hazardous inorganic contaminants in groundwater can often provide useful estimates of the maximum concentration levels that can be expected. Estimates of equilibrium concentrations within a factor of 10 or even 100 are often relevant.

Hydrolysis and Chemical Speciation

The concentrations of toxic inorganic contaminants that are reported in chemical analyses of groundwater normally represent the total concentrations of each element in solution. The concentration limits specified in drinking-water standards also are expressed in terms of total concentrations of each element or ion of interest. In aqueous systems, however, most inorganic contaminants exist in more than one molecular or ionic form. These forms, or species, can have different valences and, therefore, different mobilities in groundwater owing to different affinities for adsorption and different solubility controls. Knowledge of the distribution of species in solution is therefore necessary for consideration of the behavior of most inorganic contaminants in groundwater. The metals and metalloids are particularly prone to formation of a variety of aqueous species. These species form as a result of hydrolysis and complexation. The simple ionic species combine with ligands to form ionic or neutral-charge aqueous complexes. The major inorganic ligands in contaminated groundwater are generally Cl^-, HCO_3^-, CO_2, and SO_4^{2-} and in some cases NH_3, NO_3^-, and F^-. Even in

highly contaminated groundwater the metallic elements and metalloids are rarely present at concentrations that exceed several milligrams per liter, whereas the major ligands are commonly present at levels of hundreds or thousands of milligrams per liter. The complexation of a small percentage of a major ligand with a contaminant can result in the formation of a complex that represents a large percentage of the total contaminant concentration in solution.

Hydrolysis also influences the species of occurrence of a contaminant in groundwater. For example, dissolved Pb in water is represented by Pb^{2+} and various complexes and hydrolyzed species,

$$Pb(total) = Pb^{2+} + PbCl^+ + PbCl + PbSO_4 + PbCO_3$$
$$+ \ldots + Pb(OH)^+ + Pb(OH)_2 + Pb(OH)_3^- + \ldots \ldots$$
$$(3.11)$$

The percentage of the total Pb represented by each ligand complex depends on the equilibrium constant for each species and on the concentration of the available ligand. The hydrolysis species depend on the equilibrium constant and the pH. Computer codes such as that described by Ball *et al.* (1978) are available for speciation calculations for many metallic contaminants of interest. For some species there is considerable uncertainty in the values that are currently used to represent the equilibrium constants. Nevertheless, attempts at evaluating the species distributions are essential in investigations of the behavior of most inorganic contaminants in groundwater. If adsorption or retardation experiments are conducted in the laboratory under conditions where the contaminant of interest exhibits a much different speciation than would occur under field conditions, the laboratory result may have limited applicability to field conditions. However, if one of the major species of an element, such as Pb^{2+} in the example provided by Eq. (3.11), is limited to very low concentrations by adsorption or solubility constraints, the concentrations of complexes will also generally exist at very low concentrations except in situations where nearly all of the contaminant mass exists in the complexed form.

Oxidation and Reduction

Redox processes (i.e., oxidation and reduction) are important because they can cause changes in the mobility of many inorganic contaminants. Of the 16 inorganic constituents that, for regulatory purposes, have recommended or mandatory concentration limits in drinking-water supplies, 9 of these have more than one possible oxidation state in groundwater. These are As, Cr, Fe, Hg, Mn, Se, U, N, and S and are referred to here as the redox elements. The latter 2 elements occur in various ionic or molecular forms, such as NO_3^- and SO_4^{2-}, which are included in the drinking-water regulations. Of the remaining elements listed in drinking-water standards, 4 can be strongly influenced by redox processes even though they have only one valence state in aqueous systems; these are Ag, Cu, Cd, and Zn. The only elements in the drinking-water regulations that are relatively insensitive to the redox conditions are Cl, F, Ba, and Ra, although in some systems even Ba and Ra are influenced indirectly by the redox conditions

because of reactions with SO_4^{2-} and Fe, which are redox dependent.

The ionic or molecular forms of the redox elements in aqueous systems are commonly deduced from simplified geochemical models of equilibrium. For illustrative purposes, the results of such computations are commonly expressed as pe-pH or Eh-pH diagrams. These diagrams are ubiquitous in the geochemical literature. They are used as guides to the redox status of the aqueous system. Eh or pe can be used interchangeably through a direct numerical conversion. Each has a scale that ranges from negative to positive. Positive values indicate conditions that are more oxidizing, and negative values indicate conditions that are more reducing.

Figure 3.3 illustrates the potential for Eh and pH to control the redox state of metals and metalloids in groundwater. Diagrams such as these can be used as a conceptual guide to some of the possibilities of element behavior in groundwater. The
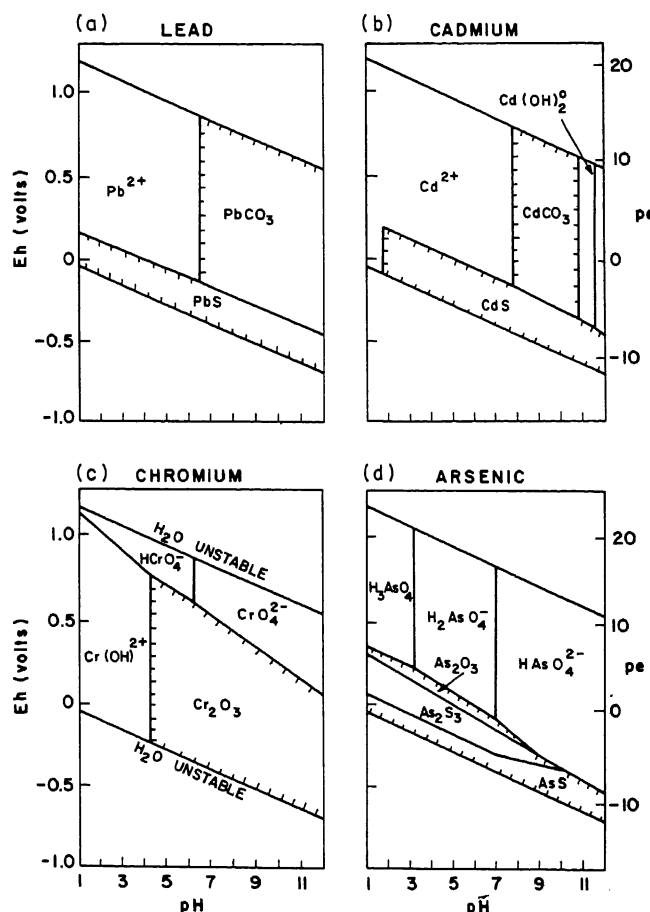
FIGURE 3.3   Eh-pH diagrams for Pb, Cd, Cr, and As for 25°C and 1 atm [from Longmire *et al.* (1982) except for Cd]. a, Pb-C-S-O-H system. Activity of dissolved Pb and S at 10^{-6} m and 10^{-3} m, respectively. b, Cd-C-S-Si system. Activity of dissolved Cd at 10^{-7} m, C = $10^{-2.5}$ m, S = $10^{-3.5}$ m, Si = $10^{-3.5}$ m. c, Cr-O-H system. Activity of dissolved Cr = 10^{-6} m. d, As-S-O-H system. Activity of dissolved As and S at 10^{-6} m and 10^{-3} m, respectively.

boundary lines between stability fields on the Eh-pH diagrams represent transition domains between the fields rather than abrupt discontinuities. In fields where solid phases are designated, the element would be expected to be immobile because of solubility constraints. In stability fields where an aqueous species is designated, this species would not be constrained by solubility if the conditions assumed for the preparation of the diagram are applicable.

Each of the four elements considered in Figure 3.3 has Eh-pH domains in which they will be immobile owing to insolubility, if equilibrium conditions are achieved. Under extremely low redox conditions, Pb and Cd, which have only one oxidation state in groundwater, form insoluble sulfide minerals. At pH levels above about 7 or 8 and at redox conditions that are not so low, these elements form insoluble carbonate minerals. Arsenic, which has two possible oxidation states in groundwater, has sulfide-mineral insolubility under very low redox conditions and does not form a carbonate mineral under any Eh or pH conditions. Cr, which also has two possible oxidation states in groundwater, forms a relatively insoluble oxide under all conditions except at very low pH or high Eh. In the absence of complexing and where solubility constraints are absent, Pb and Cd normally occur as divalent cationic species. Pb and Cd are normally relatively immobile in permeable unfractured groundwater zones. Nearly all common geologic materials have a significant capability for cation adsorption.

Of the metals and metalloids that have mandated limits specified in drinking-water standards, the four that may have the greatest potential for being relatively mobile in permeable geologic materials under Eh-pH conditions that are common in shallow groundwater are As, Cr, Se, and U. Under oxidizing conditions and normal pH conditions (see Figure 3.3) As and Cr exist as monovalent or divalent anionic species. This is also the case for Se, which has sulfide-mineral insolubility under low Eh conditions and has no severe solubility constraints under oxidizing conditions. In groundwater that has an oxidizing redox condition and has appreciable carbonate alkalinity, U in the $+6$ oxidation state occurs predominantly as anionic complexes such as $UO_2(CO_3)_3^{2-}$ and $(CO_3)_3^{4-}$. The mobility of soluble anionic species in groundwater can be limited to some degree because of adsorption. Anion adsorption is most likely to be significant when the geologic materials contain oxides of iron and aluminum. In general, there have been few field studies of the mobility or geochemical behavior of these elements in groundwater.

Although Eh-pH relations provide a framework for consideration of the behavior of redox-sensitive elements in groundwater, they do not lead directly to predictions of contaminant mobility in groundwater. To identify the condition of redox stability applicable to a particular contaminant that enters a groundwater system, one must predict the pH, Eh, and major-ion chemistry that will exist in the contaminated zone. Computer models for equilibrium water chemistry such as the one described by Parkhurst *et al.* (1980) can provide predictions of the pH and Eh, if the initial conditions and the mineral and amorphous solids that comprise the porous medium are specified. At present, however, there is little experience with which to judge the predictive capability of such models for real

groundwater systems. The usefulness of these models in many situations is also limited because of the lack of quantitative information on the influence of bacteria on redox processes in groundwater systems. It is known, however, that bacteria have an influence on the rates at which many important redox reactions proceed. A further complication is that reliable natural or contaminated-groundwater measurements of redox conditions are difficult or impossible to make because of disequilibrium or other factors.

In many contaminated-groundwater systems, dispersion can be a major influence on the redox state of the groundwater. Contaminated groundwater at waste-disposal sites commonly has a much lower initial redox state than the ambient groundwater. Dispersion commonly causes a continual mixing of waters that are different in chemical composition and in redox status. As dispersion occurs, the redox and pH conditions may change, and with these and other effects of dispersion various chemical reactions involving mineral and amorphous solids take place. These reactions can cause further changes in pH, the redox condition, the gross water chemistry, and other factors. The problem of determining the influence of dispersion on the chemical mass transfer of contaminants in groundwater is a particularly difficult one at present because the manner in which dispersion influences concentration distributions at the field scale is poorly understood, as indicated by Anderson (Chapter 2 of this volume).

Mineral Dissolution and Acid Consumption

In some situations the dissolution of minerals has a major influence on contaminant mobility in groundwater. Mineral dissolution may cause contaminant concentrations to increase if the contaminants of interest are released from the minerals as dissolution occurs, or it may cause the contaminants to be removed from solution by adsorption or precipitation if the dissolution of minerals results in changes in the water chemistry, which, in turn, cause adsorption or precipitation of other solid phases. Examples of this latter condition have been observed in aquifers contaminated by acidic leachate (pH 1.5 to 4) from mill wastes in the uranium mining districts of the western United States and northern Ontario (Taylor, 1980; Morin *et al.*, 1982). At sites in the western United States where U-mill impoundments contain ponded water or pore water at low pH, the water has exceptionally high concentrations of transition metals, heavy metals, metalloids, and radionuclides, such as ^{226}Ra, ^{210}Pb, ^{230}Th, and ^{238}U. Except for the high radionuclide concentration, similar conditions exist at many base-metal mines, where acid-leach milling occurs or where tailings become acidic because of the oxidation of pyrite.

Monitoring of plumes of contaminated groundwater in shallow unconfined sandy aquifers at leaky acidic U-tailings impoundments has established that considerable neutralization commonly occurs as the acidic water moves through the aquifers. This causes the front of the low-pH zone to advance at a rate that is retarded relative to the advance of mobile constituents such as Cl^- or SO_4^{2-}. Neutralization of the acid is attributed primarily to the dissolution of carbonate minerals, such as calcite or dolomite, in the aquifers. Using calcite as the

reactive solid phase, the neutralization process can be represented as

$$CaCO_3 + 3H^+Ca^{2+} + HCO_3^- + H_2CO_3. \quad (3.12)$$

The main species representing dissolved inorganic carbon have the equilibrium relation

$$K_{eq} = [HCO_3^-][H^+]/[H_2CO_3], \quad (3.13)$$

where K_{eq} is the equilibrium constant for the dissociation of H_2CO_3. Field and laboratory studies have established that on reaction with calcite, the pH generally rises above 6 and in some cases above 7. If neutralization causes the pH to rise above 7 nearly all of the dissolved inorganic carbon occurs as HCO_3^-, and if the pH is below 6 the dominant species is H_2CO_3. Acid neutralization also occurs as a result of the dissolution of aluminosilicate minerals, such as feldspars. It can also occur by ion exchange, when H^+ competes successfully with other cations for occupancy on exchange sites.

In cases where the acid neutralization occurs primarily by the dissolution of calcite and where the pH rises above 7, the rate of advance of the acid front can be represented in a manner similar to that depicted by Eq. (3.3) for equilibrium adsorption of trace contaminants:

$$V_a/V = 1/(1 + (\Sigma M_{CaCO_3}/\Sigma M_{H^+}) = 1/R_a, \quad (3.14)$$

where V_a is the rate of advance of the acid front, M_{CaCO_3} is the number of moles of calcite and dolomite per unit volume of porous medium, M_{H^+} is the number of moles of H^+ in the water per unit volume of porous medium, and R_a is the acid-front retardation factor.

Equation (3.14) has the same form as Eq. (3.3), and because of this similarity the acid-front retardation factor has been incorporated directly into the advection-dispersion equation in the same manner as the retardation factor for adsorption of trace contaminants. The acid-front retardation factor has been used in this manner by Haji-Djafari *et al.* (1979) and Highland *et al.* (1981) in numerical advection-dispersion simulations of the movement of acid fronts at two uranium tailings impoundments in Wyoming. Inherent in this approach is the assumption that the dissolution of calcite or dolomite occurs rapidly so that local equilibrium exists within the porous medium. If acid neutralization occurs primarily by dissolution of aluminosilicate minerals, it is much less likely that local equilibrium will occur. Whether this use of the acid-front retardation factor in advection-dispersion models provides realistic shapes for acid-front breakthrough curves cannot be determined from existing field data and has not yet been evaluated by laboratory experiments. Because the concentration of acid in solution is not dependent on the solid-phase acid neutralization capacity, it is unlikely that the shape of breakthrough curves will be closely represented by the model. The arrival of the midpoint of the breakthrough curve, however, may be adequately represented by the model.

BEHAVIOR OF ORGANIC CONTAMINANTS

Spurred by the awareness of potential environmental hazards and the development of sophisticated analytical equipment, studies of the occurrence and behavior of organic compounds in contaminated groundwater have been initiated recently. Many organic compounds are of environmental concern in part per billion (ppb) or part per trillion (ppt) quantities. Faced with these problems, research has concentrated on the 120 or so organic compounds designated as priority pollutants by the U.S. Environmental Protection Agency.

The major chemical or biochemical processes currently recognized as having a potential to be significant with respect to the occurrence and migration of these compounds in hydrogeologic regimes include sorption, chemical reaction, and biological reaction.

Sorption

Trace organic solutes, especially those that are nonpolar and relatively insoluble, tend to be sorbed by sediments and soils. For some polar organic solutes, these sorption processes are essentially electrostatic. For less polar organics the process has not been established but appears to involve weak hydrogen bonding and, more importantly, solvation or chemical partitioning similar to the distribution of solutes between two immiscible solvents. This is similar to the partitioning of solutes between oil and aqueous phases and is controlled essentially by solubility.

Sorption of organics on mineral surfaces has been documented. Field and laboratory research indicates that the sorption of organic compounds is dominantly onto particulate organic matter in the sediments. This partitioning of the solute between the aqueous phase and solid organic matter generally appears to reach equilibrium rapidly and is reversible; thus it can be introduced into the chemical mass-transfer term of the transport equation as a K_d.

The sorption of various nonionic organic solutes at trace concentrations onto sediments and soils has been shown to follow an essentially linear isotherm and to be readily reversible for a broad range of organic solute concentrations (Chiou *et al.*, 1979; Karickhoff *et al.*, 1979; Means *et al.*, 1980; Schwarzenbach and Westall, 1981). In these studies, the slopes of the linear isotherms $(K_d s)$, which are referred to by some authors as partition coefficients $(K_p s)$, were relatively independent of sediment concentration and inorganic aqueous chemistry as well. In mixtures of trace levels of organic solutes, the sorption behavior of each solute was independent of the occurrence of the other solutes in solution. In all cases, increased sorption was matched by increased solid-phase organic carbon content of the solids. When the sorption is "keyed" solely to the organic carbon content of the soil/sediment, the partition coefficient is expressed as K_{OC}, where $K_{OC} = K_p/OC$, with OC being the weight percent of solid-phase organic carbon. Karickhoff *et al.* (1979) noted that sorption on silt/clay-sized fractions was greater than the sand-sized fraction. This suggests that surface area and/or the structure of organic matter are significant variables in sorption of organic contaminants.

A promising relationship between K_{OC} and structural chemical properties of organic compounds has been developed, which permits the estimation of K_{OC} or K_p to within a factor of 10 or better for most nonpolar organic compounds. This relationship,

which involves the use of partition coefficients for mixtures of water and octanol, has been established for soils in which the organic carbon content exceeds 0.1 percent.

The development of this approach is reviewed by Hansch and Leo (1979) and others. A linear relationship exists for partitioning of organic solutes between sedimentary organic matter and groundwater and for partitioning between octanol and water. The octanol/water system can be used as surrogate for the real groundwater system in describing relative partition coefficients. The following relationships have been observed for various organic solute/sediment systems when OC > 0.1 percent:

$$\log K_{OC} = 1.00 \log K_{OW} - 0.21 \quad \text{(Karickhoff et al., 1979);}$$

$$\log K_{OC} = 0.72 \log K_{OW} + 0.49 \quad \text{(Schwarzenback and}$$
$$\text{Westall, 1981);}$$

$$\log K_{OC} = 2.00 \log K_{OW} - 0.317 \text{ (Means et al., 1980).}$$

K_{OW} is the octanol/water partition coefficient, values of which can be obtained from Leo et al. (1971) or Hansch and Leo (1979). The variation in the slope parameter may be due to differences in the sediment/soil organic matter or to differences in the organic solutes investigated.

At least three areas of uncertainty must be investigated before these partition coefficients can be used with confidence in predictive models for groundwater systems. One area is the effect of solute competition for sorption sites. Although Karickhoff et al. (1979) found that nonpolar organic solutes sorbed independently at low total solute concentration, it is likely that at some higher organic solute/solid organic matter ratio sorption will not be independent. Another problem may occur in organic-rich groundwaters such as landfill leachates. Trace organic compounds can become associated with high-molecular-weight, dissolved organic matter, often humic or fulvic acids (Schnitzer and Khan, 1972). These associated organics may not be available for sorption by matrix organic matter. Perhaps organic partition coefficients will have to be defined for a three-phase system: matrix organic matter, aqueous unassociated solutes, and aqueous humic associated solutes. As with inorganic sorption, there is a need for further theoretical description of the process and additional field data and field-scale testing for assessment of the applicability of laboratory results to field conditions.

The low K_{OW}-K_{OC} relationships described above have been determined for porous geologic materials that have appreciable contents of particulate organic carbon, such as 0.1 wt. % or more. Unfortunately, many very permeable sand or gravel aquifers may have less than this amount of organic matter. It is these aquifers in which groundwater velocities are often highest and that have the greatest potential for widespread contamination by halogenated hydrocarbons. Whether useful predictive relationships can be developed for sand and gravel aquifers with very low contents of organic carbon remains to be determined.

Although numerous investigations have shown that dissolved organic compounds at trace levels commonly exhibit linear isotherms, some organic compounds that have a potential to cause severe contamination of groundwater characteristically have nonlinear isotherms. Notable in this regard are polychlorinated biphenyls (PCBs), which are considered to have a potential to cause adverse health effects if they are present in drinking-water supplies at concentrations as low as a fraction of a part per billion (ppb) level. Relative to the levels at which PCBs are considered to be undesirable in drinking water, the solubility of PCBs is very large and ranges from approximately 50 ppb (Haque et al., 1974) to about 250 ppb, depending on the isomer that is being considered. Haque et al., who conducted batch studies of the adsorption of PCBs (Arochlor 1254) on several soils, obtained nonlinear Freundlich isotherms with the value of K_d ranging from 1.1 to 0.81. Griffen et al. (1978), who conducted batch adsorption studies (Arochlor 1242 and 1254) of three natural soil materials, also obtained nonlinear Freundlich isotherms with K_d values of between 1.5 and 0.19. These investigators noted that adsorption was favored in materials with higher organic matter and larger surface area. Because of the nonlinearity, it would be inappropriate to use Eqs. (3.2b) or (3.3) in the development of predictions of the mobility of PCBs in groundwater.

The batch adsorption studies by Haque et al. and by Griffin et al. were done with solution-phase concentrations in the range of about 5 ppb to several tens or a few hundreds of ppb. These concentration levels may be viewed as trace levels; however, they are close to the solubility limits for PCBs in water. Nonlinear isotherms are most likely to occur when the solution-phase concentration approaches the solubility limit.

Batch adsorption isotherms for many organic pesticides in a variety of soils are reported in the literature. At concentration levels much below the solubility limits, the isotherms are typically linear, and the distribution coefficients are generally large. Organic pesticides are generally considered to be relatively immobile in soil, and their use on agricultural land is rarely regarded as a significant hazard to groundwater resources. Davidson et al. (1976, 1980), however, have shown that at high concentrations several organic pesticides have very nonlinear Freundlich isotherms and, in some cases, low K_s values. Pesticides at high concentrations may occur in groundwater because of leakage of residual pesticide solutions from used containers that are deposited in road ditches, sanitary landfills, or dumps. Because millions of these containers are discarded each year, high pesticide concentrations are cause for concern.

Chemical Reactions

The major mechanisms of chemical transformation of organic compounds in aqueous systems are photolysis, oxidation, hydrolysis, and reduction. In groundwater, photolysis is not significant. Callahan (1979) compiled and assessed transformations affecting priority pollutants in aqueous systems. Only a brief, generalized discussion of the chemical reactions and the state of predictive capability is presented here.

Oxidation often requires the presence of O_2, but the reaction usually involves free radicals, especially OH., peroxy RO_2, alkoxy RO., and singlet oxygen $^1O_2$ as the oxidant. The rate of oxidation of an organic compound (OC) can be expressed in

terms of the concentration of oxidants (e.g., $[RO_2{}^0], [{}^1O_2]$) and the individual rate constants (e.g., k, RO_2):

$$-d[OC]/dt = [OC](kRO.[RO.] + kRO_2 [RO_2]$$
$$+ kHO [HO] + \ldots).$$

Prediction of the rate constants is possible for most organic compounds through the use of compiled, empirical structure-reactivity relationships (Mill, 1980). Estimates of reaction rates within a factor of 3-5 are possible. However, the free-radical content of groundwaters is essentially unknown. Prediction is then limited to approximations of relative rates of chemical oxidation.

Chemical structures most susceptible to oxidation include phenols, aromatic amines, and dienes. Saturated alkyl compounds such as alkenes, halogenated alkenes, alcohols, esters, and ketones may not be significantly oxidizable in the groundwater environment.

Hydrolysis usually involves the introduction of a hydroxyl (OH) group into an organic compound, usually at a point of unbalanced charge distribution. Hydrolysis often displaces halogens (X):

$$R'COOR + H_2O \rightarrow R'COOH + ROH,$$

$$RX + H_2O \rightarrow ROH + X.$$
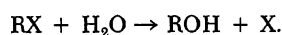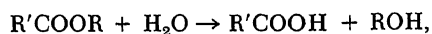
Hydrolysis may be catalyzed by acid (H^+), base (OH^-), or metal ions (M^+); thus, the rate of hydrolysis is pH and metal-ion-concentration dependent. Surface effects may also influence the rate of hydrolysis. Hydrolysis of atrazine and other pesticide derivatives is faster when humic material is present. Wolfe (1980) suggested that such catalytic processes are slow and reasonable predictions of hydrolysis rates at fixed pH could be obtained from structure-reactivity relationships that define kH for the hydrolysis rate relationship:

$$-d[OC]/dt = [OC]kH.$$

Mill (1980) felt that such a prediction could be made within a factor of 2 or 3 for specific chemicals within a family of closely related molecular structures for which rate data was available.

It is difficult to generalize relative hydrolysis rates, but the data of Mabey and Mill (1978) indicate that for halogenated hydrocarbons (RX) the hydrolysis rate increases where X is F-Cl-Br, where R changes from primary to secondary to tertiary type, and when allyl or benzyl groups were added.

Reductive dehalogenation involves the removal of a halogen atom via an oxidation-reduction reaction. Although this mechanism is not usually considered in the chemical degradation of organics it may be operative in low-redox state groundwaters. The abiological reaction requires mediators, such as Fe^{+3} or biological products to accept electrons generated by oxidation of reduced organics and to transfer these electrons to the halogenated organic to bring about dehalogenation. Esaac and Matsumuna (1980) suggested that Eh < 0.35 V is required so that electrons can be made available for dehalogenation. No studies have been made to evaluate this mechanism for organic transformation in groundwaters, but because it is operative under low-Eh conditions, it is a potentially significant process that warrants evaluation.

Biological Reactions

Enzymatic reactions brought about by the microbes inhabiting the groundwater environment may be the most important mechanism for transformation of organic contaminants. This activity is dominantly bacterial, although yeasts, fungi, and viruses may also be present. We have measured, by direct microscopic counting, 10^6 bacteria per gram of dry, sandy aquifer material in a number of landfill-leachate-contaminated groundwater systems. Although this is less than the bacteria content of fertile agricultural soils ($10^8 - 10^9$ bacteria per gram), it indicates that contaminated-groundwater systems can be microbially active.

Biodegradation of a broad range of organic compounds has been demonstrated in laboratory studies of soils, sediments, and waters. Compounds include pesticides, halogenated hydrocarbons, aromatic hydrocarbons, amines, and alcohols. The broad range of enzymatic activities in actual mixed populations of microbes permits a broad range of enzyme-catalyzed reactions (oxidation, reduction, hydrolysis, dehydration). Because the proportion of each species present at any point in space and time is environmentally dependent, predictions of actual organic transformation pathways and rates are all but impossible.

The difficulty of prediction is illustrated by the biological transformation of many chlorinated hydrocarbons, which were originally thought to be essentially nonbiodegradable (recalcitrant). It was believed that observed biogradation was limited to aerobic bacteria because anaerobic bacteria did not have sufficient energy available for biogradation because of the types of energy-yielding reactions that they could utilize. Studies of chlorinated pesticides, trihalomethanes, and other halogenated hydrocarbons revealed biodegradation in anaerobic environments. In fact, degradation of trihalomethanes was observed only in anaerobic systems (Bouwer *et al.*, 1981). In their review of microbial degradation of organics, Kobayashi and Rittmann (1982) indicated that anaerobic reductive dehalogenation may be important in transforming certain classes of organic compounds. Although there is research activity in this area, few data pertinent to groundwater systems are available at present.

The mechanisms of biodegradation of synthetic, often halogenated, organic contaminants are not well understood. Microbes that use organic compounds convert these substrates into inorganic products (e.g., CO_2, H_2S) and into cell constituents and often obtain energy for biosynthesis from these reactions. The populations responsible for such transformations increase in numbers of biomass as a result of the introduction of the organic chemical into the system. This is direct metabolism. Degradation of many synthetic organic compounds is unlikely by this direct utilization mechanism because the required enzymatic pathways have not been developed by microbes that have not been previously exposed to such organic structures. Microorganisms capable of directly utilizing DDT, 2,4,5-T, and many halogenated hydrocarbons, for example,

have yet to be isolated. However, these compounds have been observed to be biodegradable. The mechanism has been termed *cometabolism*. Microbes apparently utilize other organic substrate while performing the transformation of the organic contaminant.

Alexander (1981) points out two environmental consequences of cometabolism: (1) the responsible populations do not increase in number or biomass as a result of the introduction of the organic compound because it is not utilized for biosynthesis; and (2) a compound subject to cometabolism is modified slowly, and products structurally similar to the contaminant accumulate because the organism does not possess a sufficient array of enzymes to bring about its extensive transformation.

Considerable additional research is required before biodegradation can be adequately predicted. Correlations of organic structure and reactivity need to be improved. Models such as the biofilm-based theory of Rittmann et al. (1980) need to be improved by incorporation of in situ parameters and by evaluation at a number of field sites.

It must be pointed out that microbial processes can also increase groundwater toxicity as well as reduce it. Biodegradation of toxic organics such as DDT can produce more toxic intermediate products such as DDE. Also, microbial methylation of metals such as mercury and lead has been shown to increase the metals' toxicity to other organisms.

Organic Compounds as Complexing Agents

Complexation of some inorganic contaminants, such as trace metals, by inorganic ligands (e.g., CO_3^{2-}, OH^-) has been discussed with respect to chemical speciation. Cationic inorganic contaminants may also be complexed by organic ligands. Many such complexes are stable in groundwater. Although most predictive models include inorganic complexes in consideration of aqueous speciation and transport, the effects of organic ligands are usually not included. Models considering the possible influence of simple organic ligands such as NTA, citric acid, and EDTA on the chemical speciation in seawater or freshwater have produced conflicting indications of the importance of these organic ligands. Organic complexation should increase as the concentration of organic ligands increases and is expected to be significant in groundwaters with high dissolved organic carbon (DOC).

The transport of inorganic contaminants as organic complexes has been documented. Means et al. (1978) reported unexpected mobility of ^{60}Co and U from liquid disposal sites at the Oak Ridge National Laboratory. Apparently, ^{60}Co and some U were complexed by EDTA that was a constituent in wastes from decontamination facilities and by dissolved humic substances. The neutral or anionic species so formed were not subject to the expected retardation by adsorption onto the soil. Iron, toxic trace metals, and other radionuclides have been reported to be transported as organic complexes in groundwaters and surface waters.

Prediction of the extent of organic complexation in contaminant transport is limited by the lack of knowledge concerning the nature and content of organic ligands in groundwaters and

by the lack of a comprehensive thermochemical data base for complex ligands. A majority of organic ligands are natural, high-molecular-weight, structurally complex fulvic and humic acids. Assuming that these ligands dominate the groundwater DOC and that they have properties similar to analyzed material (Schnitzer and Khan, 1972), the complexing capacity of groundwaters can be calculated as 1×10^{-2} to 5×10^{-2} meq/L for each 1 mg/L of DOC. It is expected that most of this complexing capacity is taken by major cations and that only a part is available to trace metals or radionuclides. The potential for significant complexation of trace metals, for example, has been demonstrated in high-DOC groundwaters contaminated by landfill leachate (Knox and Jones, 1979). Prediction of inorganic contaminant complexation by complex organic ligands has been attempted through models that simplify the organic-metal interaction (Sposito, 1981), but the applicability of these models for application to contaminated-groundwater systems has yet to be assessed.

FIELD STUDIES OF CONTAMINATED GROUNDWATER

Although most of the literature on the chemical behavior of contaminants in groundwater is based on batch and column experiments and on thermodynamic models, insight pertaining to contaminant behavior is also obtained from field investigations of zones of contamination. In favorable circumstances data from existing zones of contamination at waste-disposal or chemical spill sites can be used to assess the applicability of predictive models.

There are 10 inorganic constituents for which maximum contaminant levels are specified in the National Interim Primary Drinking Water Regulations of the U.S. Environmental Protection Agency (1975). These are As, Ba, Cd, Cr, F, Pb, Hg, NO_3^-, Se, and Ag. Except for NO_3^- and Cr, these constituents are rarely reported as a cause of significant deterioration of groundwater quality.

Nitrate is a particularly serious cause of groundwater contamination. NO_3^-, which has a maximum permissible concentration of 10 mg/L as N_2 in drinking water, is a common cause of groundwater-quality deterioration because nitrogen is a major component of agricultural fertilizer and of animal and human wastes and because nitrogen commonly occurs as NO_3^-, which is very soluble and generally unretarded by adsorption. The widespread nature of NO_3^- sources and the mobility of NO_3^- cause unconfined aquifers to be particularly susceptible to gradual long-term increases in NO_3^- concentrations. Increases will probably continue because the quantity of NO_3^- available for entry into the groundwater zone will probably not diminish appreciably in the next few decades. To cause a decrease would require widespread changes in agricultural practice and in the management of animal and human sewage.

It is fortunate that in at least some groundwater systems there exists a biogeochemical process, namely denitrification, that tends to ameliorate the influence of NO_3^- inputs to the groundwater zone. The denitrification process can be expressed

schematically as

$$NO_3^- + \text{organic carbon} \rightarrow N_2 + CO_2 + H_2O.$$
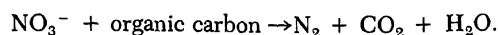
According to thermodynamic data, denitrification is expected to occur only in zones that are essentially devoid of dissolved oxygen (Lindsay 1979). However, field studies have established that it will occur in groundwater zones where labile organic matter and denitrifying bacteria exist even if the groundwater contains low but measurable concentrations of dissolved oxygen (Gillham and Cherry, 1978). Although groundwater from wells in zones where denitrification apparently occurs contains detectable quantities of dissolved oxygen, it is likely that the reduction of NO_3^- takes place in microenvironments in small pores or on grain surfaces where the redox conditions are most suitable. Organic matter is a source of energy and of cell carbon for the bacteria that mediate the reduction process.

The loss of NO_3^- in the groundwater zone due to denitrification cannot be predicted simply from measurements of the redox condition of groundwater samples. Based on laboratory-column experiments, Doner and McLaren (1976) developed a mathematical expression to describe steady-state NO_3^- loss in sandy soils due to denitrification. The expression contains several parameters, including the mass of N utilized per unit biomass per unit time for maintenance of the bacterial population, the mass of N utilized per unit biomass in wasted bacterial metabolism, and the mass of organic matter available to the bacteria that mediate the reaction. The work by Doner and McLaren demonstrated the importance of bacteria and organic matter in the denitrification process. It is unlikely, however, that mathematical expressions derived from laboratory experiments will be of much use in the development of predictions of denitrification in the groundwater zone. Whether the microbiological conditions that are critical to the denitrification process in the field can be adequately represented in the laboratory remains to be determined. The development of field techniques for the in situ measurement of the main rate-determining factors is desirable.

Of the other nine inorganic contaminants, Cr has probably caused the most degradation of groundwater. Cr is used in many manufacturing processes and is a constituent in sewage sludge. Cr that leaks from waste lagoons or that leaches from industrial landfills and sludge-disposal areas or from soil contaminated by spills of Cr-rich liquids can pose a hazard to groundwater quality.

Shallow aerobic groundwater zones are particularly susceptible to contamination by Cr(+VI) because under oxidizing conditions the stable Cr species ($HCrO_4^-$ or CrO_4^{2-}) are relatively soluble (Figure 3.3) and undergo little retardation by adsorption in many types of permeable geologic deposits. Perlmutter and Lieber (1970) and Pinder (1973) have described a major occurrence of Cr(+VI) contamination in a sand aquifer on Long Island, New York. The zone of contamination is approximately 1400 m long, 350 m wide, and 25 m thick. Shallow zones of Cr(+VI) contamination in sand aquifers have recently been one of the main subjects of legal proceedings related to groundwater protection legislation in the state of Michigan. Cr(+III) is not a cause of significant groundwater contamina-

tion because the Cr(+III) is insoluble in water except at low pH and because it occurs as cationic species that are absorbed.

Of the other eight inorganic contaminants, a few have such severe solubility limitations that they are generally immobile in groundwater under normal pH conditions. For example, the concentration levels at which Ba can occur are limited to very low levels by the solubility of $BaSO_4$. Two of the contaminants, Hg and Ag, rarely cause groundwater contamination because they are uncommon constituents in waste materials deposited on land and because their mobility in normal groundwater conditions is probably limited by solubility constraints and adsorption. The remaining contaminants—As, Cd, F, Pb, and Se—have been reported in only a few areas as causes of severe local groundwater degradation. Some of these contaminants are particularly prone to causing groundwater contamination in situations where the pH is much lower or much higher than the normal range for groundwater. Conditions of extreme pH in groundwater are common in waste materials at metal or uranium mines or in ash disposal areas associated with coal-fired power plants. Se and As, for example, have been reported at exceptionally high concentrations in groundwater at fly-ash disposal sites in North Dakota in zones where pH levels are above 10 (Groenewold et al., 1981). In contrast, similar investigations at fly-ash disposal sites in southern Ontario, where the pH of the groundwater is between 7 and 9.5, have established that the concentrations of these elements and the other elements with maximum permissible limits specified in drinking-water regulations are low (Dodd et al., 1981).

Field investigations of contaminated aquifers at uranium tailings impoundments in Wyoming and in northcentral Ontario (Morin et al., 1982) have established that the contaminated zones at low pH (i.e., generally less than about 4.5) invariably have high concentrations of many transition metals, heavy metals, metalloids, and radionuclides, whereas the neutral pH zones of contamination that exist in advance of the retarded low-pH fronts rarely have any of these constituents at levels above the drinking-water limits. This is the case because pH exerts a dominant influence on the solubility controls and the adsorption of these contaminants. The hydrogeochemical nature of sandy aquifers that receive acidic water from tailings impoundments can be represented as three main zones: the acidic zone, the neutralization zone, and the neutral-pH zone. In the neutralization zone, the hazardous contaminants are transferred from the water phase to the solid phase by precipitation and adsorption. In the prediction of the movement of metals and radionuclides in groundwater systems that are receiving acidic, metal-rich, or radionuclide-rich water, the critical task is the prediction of the advance of the front of the acidic zone. Field investigations, e.g., Morin et al. (1982), have shown that low pH fronts can be greatly retarded because of reactions with porous media, but the development of a methodology to predict neutralization-zone behavior at new sites is in the early stages.

A potential cause of groundwater contamination that is an issue of concern in many communities is municipal landfills. Detailed monitoring of zones of contaminated groundwater has taken place at landfills on permeable deposits of sand and gravel on Long Island (Kimmel and Braids, 1980) in Ontario (Cherry,

1983), in Delaware (see Chapter 10 of this volume), and at many other locations in North America. The investigations indicate that, although major ions such as Cl^-, HCO_3^-, Na^+, Ca^{2+}, and Mg^{2+} and minor constituents such as NH_4^-, Fe, and Mn are mobile, the toxic inorganic constituents generally do not occur at concentration levels above the mandatory drinking-water limits. At the Ontario sites, no values above the limits were reported for toxic inorganic constituents. At the Long Island sites only Se occurred in some samples at levels slightly above the limit. At all of these sites, the pH values of the zone of contaminated groundwater were near neutral.

The leachate from municipal landfills has high concentrations of dissolved organic compounds. However, despite the potential for mobilization of toxic inorganic compounds by complexing with organic compounds, immobility of the heavy metals and metalloids is the rule rather than the exception.

In some contaminated groundwater, mineral dissolution occurs because the contaminant solution that invades the porous medium causes reduction of Fe or Mn. This is particularly the case when the invasion takes place at shallow depth where Fe and Mn occur in the porous medium as oxides of $Fe(+III)$ and $Mn(+IV)$. When the water in the reduced state encounters the oxides, they become unstable and the Fe and Mn go into solution as $Fe(+II)$ and $Mn(+II)$. Their solubility in the reduced oxidation states can be high. Oxides of $Fe(+III)$ and $Mn(+IV)$ are natural scavengers of metallic elements in the geochemical environment, and, therefore, their dissolution can cause the release of elements that accumulated in the oxides under natural conditions before the invasion of the contaminant solution. An example of the influence of this source of metals on the chemistry of contaminated water beneath a landfill is described by Suarez and Langmuir (1976). The importance of these oxides as metal scavengers is described by Jenne (1968, 1977).

It has only been in recent years that increased concern for groundwater quality and the availability of greatly improved analytical methods for the identification of organic compounds has resulted in appreciable monitoring of toxic or potentially toxic organic contaminants in groundwater. This work is revealing widespread contamination of groundwater by organic chemicals, which indicates significant mobility of many of these substances through soil and in the groundwater zone. Some specific examples (Wilson *et al.*, 1981) are occurrences of trichloroethane in many groundwaters in the United States and Europe as a result of spills, leaks, and disposal of wastes in soil; occurrence of 1,2-dibromo-3-chloropropane in groundwater in areas in California, where it was applied to soils as a nematocide; contamination of a large body of groundwater by phenol in the vicinity of an accidental spill of this compound in Wisconsin; and the movement into groundwater of 4,4'-methylene bis(2-chloroaniline) from a wastewater lagoon in Michigan.

The processes that control the behavior of specific organic contaminants in groundwater have been evaluated at only a few field sites. One such study was conducted during injection of tertiary-treated sewage effluent in a sand aquifer near Palo Alto, California (Roberts *et al.*, 1980). It was observed that organic trace contaminants under anaerobic conditions were attenuated to varying degrees during the passage of the treated effluent through the groundwater zone. Of the various low-molecular-weight halogenated organics studied, chlorobenzene was most mobile but traveled at a rate of approximately 1/36th of the rate of nonadsorbed inorganic constituents. Dichlorobenzene isomers and 1,2,4-trichlorobenzene isomers were apparently more strongly adsorbed than chlorobenzene. Naphthalene showed evidence of biodegradation. Another injection study is under way in southcentral Ontario in an aerobic zone in a sand aquifer containing a very low solid-phase organic carbon content (MacKay *et al.*, in press). At this site, 12,000 L of water containing chloride and bromide salt as nonreactive tracers and containing five toxic halogenated hydrocarbons (o-dichlorobenzene, bromoform, carbon tetrachloride, hexachloroethane, and tetrachloroethylene) were injected during a 14-h period as a slug into the aquifer. The behavior of the salt tracers and the organic compounds under natural flow conditions was monitored for more than a year following the injection. Two of the compounds (carbon tetrachloride and bromoform) were found to be quite mobile; they traveled at a rate of about two thirds of the groundwater velocity. Tetrachloroethylene traveled at a rate of about one third of the groundwater velocity and o-dichlorobenzene and hexachloroethane at a rate of less than a quarter of the groundwater velocity. The first three compounds above were not noticeably biodegraded. There is a possibility that the latter two compounds were biodegraded to some degree, however, at most very slowly.

At the above-cited landfills on Long Island and Ontario, landfill-derived, dissolved organic carbon exists throughout the zones of contaminated groundwater. Investigations of the identifiable compounds in this dissolved organic fraction indicated that many toxic or potentially toxic compounds are mobile in these groundwater systems (Reinhard *et al.*, in press). Even with modern analytical techniques, only organic compounds that comprise as much as 5 to 10 percent of the DOC in zones of contaminated groundwater at landfill sites are identifiable. It is expected that toxic organic contaminants are mobile in groundwater at many municipal landfills situated on permeable deposits. The dissolved organic fraction in contaminated groundwater at landfills has a much greater potential to cause severe contamination of groundwater resources than dissolved inorganic contaminants.

CHEMICAL REACTIONS AND PERMEABLE MEDIA

The degree to which chemical reactions can cause attenuation of contaminants in groundwater can be dependent on the type of permeable media in which the contaminants occur. In this chapter the discussions pertain implicitly to nonindurated porous media such as gravel, sand, silt, or clay in which contaminants are transported by groundwater flow through the pore spaces between the grains or particles that comprise the media. The advection-dispersion theory and the isotherm approach to predictive modeling of the behavior of adsorbed contaminants were developed specifically for this type of medium. In many regions of North America, the occurrence and movement of

contaminants in other types of permeable media such as fractured rock or fractured fine-grained, nonindurated deposits are also important. The effects of chemical processes in these deposits can be very different from those that occur in porous media.

In groundwater systems in fractured crystalline rock in which the rock matrix is relatively nonporous (such as granite, marble, and many other types of igneous and metamorphic rocks), the migrating contaminants contact only the mineral surfaces exposed on the fracture walls and the amorphous geochemical weathering or alteration products that exist on these surfaces. Measurement of adsorption parameters for predictive modeling is particularly difficult for this type of medium because the measurements must adequately represent the conditions that occur on the surface of the fractures as they exist in the groundwater zone. The distribution coefficient expressed in the normal manner relative to the mass of solids is inappropriate because rock mass and fracture surface area have no known general relation. For this reason the distribution coefficient for fractured crystalline rocks has been defined in terms of the effective surface area of reaction in the fractures. There have been few attempts to determine the adsorptive properties of relatively undisturbed fracture surface, and there have been no assessments under field conditions of the predictive capabilities of the models using parameters determined by the existing measurement techniques.

The flow of groundwater in fractured porous media such as weathered deposits of silt or clay or fractured rocks that have considerable intergranular porosity such as shale and porous sandstone commonly occurs through the fractures. Little or no flow takes place in very porous but relatively impermeable matrix. As contaminants are transported through the fracture network, transient chemical-concentration gradients exist between the water in the fractures and the pore water in the matrix. These gradients cause the contaminants to diffuse into the matrix in the frontal part of the contaminant zone and diffuse out of the matrix in the trailing part. Models of the advection, dispersion, and diffusion of contaminants in fractured porous media have established that diffusion into the porous matrix can have a strong influence on contaminant behavior (Tang *et al.*, 1981; Grisak and Pickens, 1981). The surface area that controls adsorption is generally the surface area contacted by the contaminants in the porous matrix, which is many orders of magnitude larger than the surface area of the fracture surfaces. The chemistry of the groundwater in the porous matrix can have a dominant effect on chemical mass transfer by precipitation or dissolution. The bacterial population that exists in the porous matrix may be more important than exists on the fracture surfaces. Research pertaining to the chemical and biochemical behavior of contaminants in fractured porous media is in its infancy.

SUMMARY AND CONCLUSIONS

Most of what is known about the chemical behavior of contaminants in groundwater pertains to inorganic contaminants. The two main approaches used for the prediction of the chemical

behavior of inorganic contaminants in groundwater involve the use of the distribution coefficient, which is incorporated in a simple retardation term into the advection-dispersion equation, and the use of thermodynamics-based chemical equilibrium models. When the contaminant of interest exhibits a linear equilibrium adsorption isotherm, the retardation relation can be used to estimate the relative rate of advance of the mid-concentration position of the front of the contaminant zone. This approach is applicable in situations where contamination emanates from a continuous source. It can also be used to estimate the center of the mass of the contaminant zone in situations where the contamination originated from a distinct temporary source. Field experiments have shown that for trace-level inorganic contaminants controlled by adsorption, such as some cationic radionuclides, the retardation relation, when applied in favorable circumstances, provided estimates of relative velocity within a factor of about 5 or better. The usefulness of this approach for prediction of the relative advance rates of toxic nonradioactive inorganic or toxic organic contaminants in groundwater has not yet been subjected to a comprehensive evaluation.

When the retardation relation is incorporated into one-dimensional advection-dispersion models, simulated breakthrough curves for column experiments using adsorbed tracers that have linear isotherms do not agree closely with experimental data. The experimental breakthrough curves are distinctly asymmetrical, whereas the simulated curves are symmetrical or nearly symmetrical. Hypotheses to account for this discrepancy have not yet been subjected to comprehensive evaluation. This area of uncertainty and the uncertainties associated with sample disturbance and related geochemical effects do not bode well for predictions of the first arrival of fronts or of the tails of zones of adsorbed toxic contaminants.

The maximum concentration levels at which many inorganic contaminants occur in groundwater is controlled by the solubility of minerals or other solids. Thermodynamic-based equilibrium models are available for prediction of these maximum concentrations in groundwater in which dissolved organic matter is not a complicating factor. Although the thermodynamic data for many of the solid phases and complexes of relevance are questionable, and although equilibrium is probably not achieved in many situations, these models can provide useful order-of-magnitude estimates of maximum possible concentration levels. The models can be used to assess the possible influences of various geochemical scenarios on the occurrence of inorganic contaminants in groundwater. Although the most advanced equilibrium geochemical models that are currently available have well-developed computational capabilities for complex inorganic aqueous systems, they are static models in that they do not include formal representations of the effects of advection or dispersion. Advanced models of this type have not yet been incorporated into advection-dispersion models, although the effects of advection and dispersion have been approximated by the use of equilibrium models in combination with cell models.

The chemical behavior of most toxic inorganic contaminants depends strongly on the redox and pH conditions of the contaminated groundwater. When the pH is very low or very high,

some heavy metals or metalloids are commonly mobile. A very low redox condition generally promotes immobility. Field investigations have established that, at neutral pH, metals and metalloids are not commonly mobile, except for Cr(+VI) and Se, which occur in anionic forms and tend to be mobile when oxidizing conditions prevail. The most critical task in the prediction of the chemical behavior of most toxic inorganic contaminants is the prediction of the pH and redox conditions. This necessitates prediction of the gross water chemistry of the migrating zone of contamination. In addition to the influence of geochemical factors, the gross water chemistry is affected by dispersion, which often causes mixing of waters of different pH and redox status as the zone of contamination moves through the groundwater system. The task of predicting the chemical behavior of reactive inorganic contaminants therefore cannot be isolated from the problems inherent in predictions of dispersion in the groundwater zone.

Dissolved organic contaminants in groundwater can be influenced by adsorption, oxidation, hydrolysis, or microbial degradation. Laboratory experiments indicate that many trace organic compounds exhibit linear adsorption isotherms and, therefore, may be favorable for transport simulation using advection-dispersion-retardation models. Considerable success has been achieved in estimating, from solubility data, the distribution coefficients for adsorption of halogenated hydrocarbons by solid organic matter in porous geologic materials that have appreciable organic matter. The other processes that can cause attenuation of dissolved organic compounds are much less amenable to quantification, particularly for anaerobic groundwater where biological transformations are poorly understood. The current paucity of information on the chemical and biochemical behavior of organic compounds in groundwater is a particularly serious liability in the assessment of future changes in groundwater quality because entry of organic compounds to the groundwater zone is now common and because many toxic organic compounds are relatively mobile.

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III

METHODS OF
WASTE DISPOSAL

Shallow Land Burial of Municipal Wastes

4

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ABSTRACT

Environmental laws and regulations promulgated since the early 1960s have increased the use of the sanitary landfill and changed its character. Total isolation of wastes from the environment is not possible; some migration of leachate from wastes buried in the ground will always occur. Disposal sites should be judged on a site-by-site basis rather than by rigid criteria for site selection and design. The performance should take into account several factors: (1) the nature of the wastes; (2) the site hydrogeology, including a complete water balance; (3) the attenuation of contaminants by geologic materials; and (4) the release rate of unattenuated contaminants to surface waters or groundwaters.

In recent years there has been a trend away from numerous, small disposal sites toward fewer and larger sites. Large disposal sites increase the environmental stress, since the attenuation capacity of the geologic material has a finite, though generally not well-defined, limit. Fine-grained geologic materials, which have low hydraulic conductivities and attenuating characteristics considered favorable for waste disposal, are geologic conditions generally considered suitable for disposal of wastes. Landfill covers are, perhaps, the least regulated engineered part of sanitary landfills, yet they are critical in controlling leachate migration and the water balance. Also, the role of migration in the unsaturated zone is often overlooked, especially in humid areas.

INTRODUCTION

The environmental effects of land disposal are difficult to determine because the subsurface is complex and we do not understand it well enough to be able to describe it completely and monitor it properly. Studies of the hydrologic systems in fine-grained geologic materials—into which current disposal practices direct most wastes—were almost nonexistent 20 years ago. However, during the past two decades, studies of fine-grained materials have developed methods to provide the data required to study waste-disposal sites (e.g., Farquhar and Rovers, 1975; Griffin *et al.*, 1976, 1977; Cartwright *et al.*, 1981). Today, this is a highly active field of research, and it is nearly impossible to keep up with all the scientific literature. Many

disposal sites have been studied that document the chemical and physical changes that can occur in the earth materials as a result of the burial of waste. Land disposal of solid wastes—domestic and industrial—has been practiced for many years; over the past 30 to 40 years the open burning dump has gradually been replaced by the sanitary landfill. Garland and Mosher (1975) estimated that in 1973 there were about 14,000 operating sanitary landfills in the United States, and Clark (1975) estimated that about 240 were operating in Illinois in 1973 (down from the more than 2000 known disposal sites a decade earlier). This reduction in the number of operating landfills—typical throughout the United States—has effectively concentrated increasing volumes of refuse at fewer sites, especially near the urban center.

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The ever-increasing volume of waste generated by humans can be placed in the air, water, and land. The increasingly strict regulations, passed in the 1960s and 1970s and governing the discharge of pollutants to the air and surface water, placed increased emphasis on land disposal. This was only natural considering the public awareness of air and water pollution and the very clear dangers if past practices continued. Since there are interchanges between the three media, land disposal of waste ultimately discharges some of the waste products back to the water or air. It is interesting to note that the success of land disposal is judged primarily by the rate of return of the pollutants to the air or water. A thoughtful discussion of land disposal of wastes was published by the American Society for Testing and Materials (ASTM) Subcommittee D18.14 (1981). One characteristic of the sanitary landfill is the potential for production of large amounts of leachate and gas (Pohland, 1980). The environmental consequences of the leachate and gas production have received considerable attention. This concern, in turn, has led to a variety of developments for control and treatment, including the concept of total isolation. The degree of control and treatment required is a function of the environmental sensitivity of the site and the degree of uncertainty acceptable.

LEACHATE CHARACTERISTICS

In the case of most municipal landfills, leachate is produced when infiltration from rainfall, surface drainage, and/or ground-

water inflow combine with the moisture already in the waste to exceed the liquid holding capacity (full capacity). In some cases, the compaction processes used at landfills may squeeze sufficient moisture from the refuse to exceed the liquid holding capacity and cause leachate movement prior to infiltration of moisture.

There are only limited data on sanitary landfill leachate characteristics (Table 4.1). There are three main variables controlling the leachate characteristics: (1) the variability of the waste itself, (2) the climatic and hydrogeologic setting, and (3) time. The available data show the variability of leachate characteristics from site to site and from time to time. The recognition of the variability of the characteristics with time offers potential for innovative control measures and treatment practices.

GAS PRODUCTION

The principal gases produced by sanitary landfills (in addition to the obnoxious odor) are potentially explosive mixtures of methane (CH_4) and acidification of the groundwater due to the solution of carbon dioxide (CO_2). Methane is considered to be the greatest problem since the acidification problem is generally easily overcome by the natural buffering capacity of most geologic materials.

Farquhar and Rovers (1973) studied the pattern of gas generation of a "typical" sanitary landfill (Figure 4.1). They identified four phases: Phase 1, aerobic; Phase 2, anaerobic non-

TABLE 4.1 Characteristics of Leachate and Domestic Waste Waters

Constituent	Range[a] (mg/L)	Range[b] (mg/L)	Range[c] (mg/L)	Leachate[d] Fresh	Leachate[d] Old	Wastewater[d]	Ratio[d]
Chloride (Cl)	34-2,800	100-2,400	600-800	742	197	50	15
Iron (Fe)	0.2-5,500	200-1,700	210-325	500	1.5	0.1	5,000
Manganese (Mn)	0.06-1,400	—	75-125	49	—	0.1	490
Zinc (Zn)	0-1,000	1-135	10-30	45	0.16	—	—
Magnesium (Mg)	16.5-15,600	—	160-250	277	81	30	9
Calcium (Ca)	5-4,080	—	900-1,700	2,136	254	50	43
Potassium (K)	2.8-3,770	—	295-310	—	—	—	—
Sodium (Na)	0-7,700	100-3,800	450-500	—	—	—	—
Phosphate (P)	0-154	5-130	—	7.35	4.96	10	0.7
Copper (Cu)	0-9.9	—	0.5	0.5	0.1	—	—
Lead (Pb)	0-5.0	—	1.6	—	—	—	—
Cadmium (Cd)	—	—	0.4	—	—	—	—
Sulfate (SO_4)	1-1,826	25-500	400-650	—	—	—	—
Total N	0-1,416	20-500	—	989	7.51	40	25
Conductivity (μmhos)	—	—	6,000-9,000	9,200	1,400	700	13
Total dissolved solids	0-42,276	—	10,000-14,000	12,620	1,144	—	—
Total suspended solids	0-2,685	—	100-700	327	266	200	1.6
pH	0.7-8.5	4.0-8.5	5.2-6.4	5.2	7.3	8.0	—
Alkalinity as $CaCO_3$	0-20,850	—	800-4,000	—	—	—	—
Hardness total	0-22,800	200-5,250	3,500-5,000	—	—	—	—
Biological oxygen demand	9-54,610	—	7,500-10,000	—	—	—	—
Chemical oxygen demand	0-89,520	100-51,000	16,000-22,000	22,650	81	500	45

[a]U.S. Environmental Protection Agency (1973).
[b]Stein et al. (1971).
[c]U.S. Environmental Protection Agency (1975).
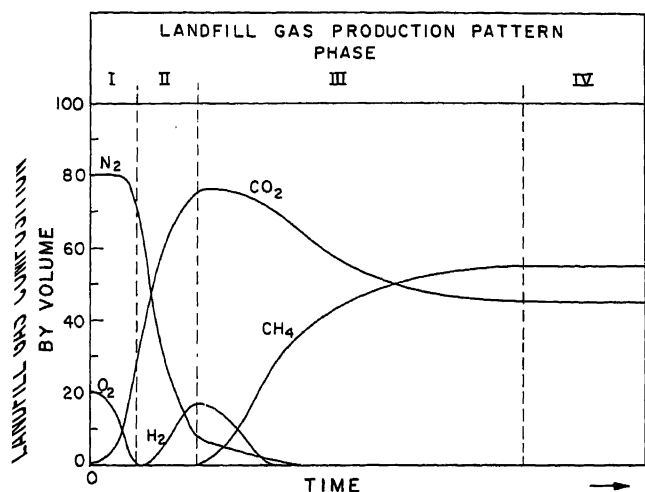[d]Brunner and Carnes (1974).

FIGURE 4.1   Sanitary landfill gas production pattern (from Farquhar and Rovers, 1973).

methanogenic; Phase 3, anaerobic methanogenic, unsteady; and Phase 4, anaerobic methanogenic, steady. The nonmethanogenic stage is initiated by hydrolytic processes by reducing complex organic matter to soluble components by means of cellular enzymes. The microorganisms in the methanogenic stage are generally considered common bacterial inhabitants of soil and sewage.

The gas generation is controlled by refuse composition, moisture, temperature, alkalinity, and pH (see Figure 4.2). The rate of gas production and the length of each of the initial three phases vary considerably, depending on conditions. Most sanitary landfills will reach stable CH_4 production (Phase 4) in 180 to 500 days (Farquhar and Rovers, 1973). The initial phases may only be a few days to weeks in length.
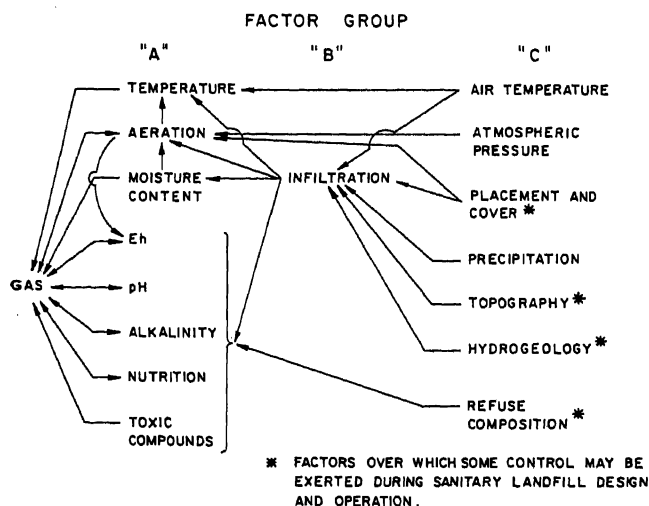
FIGURE 4.2   Factors affecting gas production in sanitary landfills (from Farquhar and Rovers, 1973).

Conditions may be such as to allow gas generation, but there may be nutritional deficiencies in the refuse, which impede the microbial population and slow gas production rates. Also, it is certain that there are many materials that are toxic or inhibitory to gas-producing microorganisms, which could be disposed of into sanitary landfills.

Moisture content is perhaps the most interesting controlling factor. Moisture is critical to gas generation. Gas production increases in sanitary landfills with moisture content up to saturation. With saturation and a rise in the water table up through the refuse, gas generation is reduced, especially the production of CH_4. This in part explains the lack of gas problems at many older landfills in humid environments.

HYDROGEOLOGIC CRITERIA

Regulations governing the disposal of wastes—including hazardous wastes—are designed to protect human health and ensure the quality of our water resources. It is unrealistic to assume that rigid geologic and hydrogeologic criteria can be applied over the entire United States or even to a single state. Strict application of some criteria, such as the depth from the bottom of the waste to the water table, can actually lead to the selection of unsuitable sites. Regulations governing the disposal of wastes should be applied on a site-by-site basis and should provide performance standards that the disposal site must meet. In evaluating a site, the possible effect on the environment is the most important consideration. In addition, the specific character of the wastes, the geologic materials at the proposed site, and their interaction must be carefully examined.

Each regulatory agency has different rules, regulations, and guidelines that categorize wastes and landfills according to the type of wastes to be received, geologic setting, or engineering specifications. For example, landfill sites in Illinois are divided into five classes on the basis of geologic and groundwater conditions. Illinois regulations require disposal of hazardous wastes in class I and possibly class II sites. Class I sites require a permeability barrier at the bottom and sides of the trenches consisting of 10 ft of material with a hydraulic conductivity of 1×10^{-8} cm/sec or less; class II sites require the same thickness of material, but the material must have a hydraulic conductivity of 5×10^{-8} cm/sec or less. No standard specifications are given for making this measurement, but ASTM (1970) does have a suggested laboratory method. Laboratory measurement of such low values is difficult; the error in measurement may be quite large (see Figure 4.3), possibly greater than the difference that distinguishes the classes of sites. Field measurement is also difficult, time-consuming, and costly and may be no more accurate than laboratory measurement. Current Illinois Environmental Protection Agency (IEPA) guidelines require, in addition to the specified permeability barrier at the bottom and sides of trenches, a minimum of 500 ft separating the waste from the nearest water well or body of surface water.

These and other hydrogeologic requirements (such as required depth from the trenches to the water table) are subjective; some are based on misconceptions rather than on scientific principles. For example, there is little point in regulating

Idealized stratigraphic column

Depth (ft)		Material	Average texture (%) sand-silt-clay	Hydraulic conductivity (cm/s) Field Test[1]	Hydraulic conductivity (cm/s) Lab Test[2]
0		Peoria Loess	5-65-30		1.1×10^{-6}
		Roxana Silt			
10		Sangamon Soil	30-35-35	4.4×10^{-7}	1.6×10^{-7}
		Vandalia Till (ablation)	45-40-15	$4.1 \times 10^{-5} - 2.3 \times 10^{-4}$	2.0×10^{-7}
20		Vandalia Till (basal) fractured, few sand lenses	41-40-19	2.0×10^{-4}	2.0×10^{-7}
30					
40					
50		Vandalia Till (basal) few sand lenses	38-43-19	4.4×10^{-7}	4.1×10^{-9}
60					
70		Banner Fm. (till)	10-50-40		
80					
90					
100		Pennsylvanian shale			

[1] Water injection/recession curve tests by ISGS

[2] Samples recompacted

FIGURE 4.3 Comparison of field and laboratory hydraulic conductivities at Wilsonville, Illinois (from Johnson et al., 1983).

the distance between a landfill and a water well unless other factors critical to the protection of the well (such as well construction, well depth, groundwater gradient, and the hydraulic conductivity of the intervening earth materials) are also considered in the regulation.

A performance standard should stipulate the maximum effects disposal can have on surrounding land uses. For example, a standard might be written to limit the volume and concentration of the contaminant allowed to be discharged from the landfill and specify the water-quality criteria as related to a specific water use and/or the degree to which ambient water quality can be altered. The performance standard can be a general statement specifying drinking-water standards or designating specific-ion concentrations, or a combination of both. The standard should clearly specify the area at which the criteria for water quality are to be applied (such as at the property line or the nearest aquifer or body of surface water). If a mixing zone is acceptable (as in the case of a point-source discharge into surface water), then the performance standard should specify the size of that zone. These specifications must be realistic; specifying that there must be a "zero discharge" immediately adjacent to the waste is not realistic.

The performance standard presumes that it can be demonstrated in advance how fast and where the contaminants will

travel and that both retardation and mobilization factors are known. In fact, this is imperfectly known, and estimates are all that is available. However, predictions can be verified through the proper design of the monitoring system. Methods discussed in many chapters of this volume deal directly with methods to predict contaminant transport.

To promulgate guidelines or regulations using design criteria, a regulatory agency must be sufficiently knowledgeable in its field to ensure that the particular method or design specified is the only appropriate means of achieving the desired result. In waste disposal, we generally do not have sufficient knowledge to stipulate method or site characteristics that apply consistently. Thus, where design criteria are stipulated, deficiencies are generally present in regulations and guidelines. Each site will be different and must be considered on a site-by-site basis.

Unsaturated Flow

Unsaturated flow of groundwater has only recently been recognized as an important factor in contaminant transport by geologists and engineers engaged in waste-disposal work. The field of soil physics has made great progress in the past 20 yr; however, little is known about this field by many practicing hydrogeologists. This was shown by the design of french drains for landfills, such as at Sheffield, Illinois (Dragonette *et al.*, 1979), where the principles of unsaturated groundwater flow were not utilized, resulting in nonfunctioning drains.

We must also consider the vapor transport of contaminants with the landfill gases. Such transport could be very rapid.

Johnson and Cartwright (1978, 1980) reported on studies of sanitary landfills in the unsaturated zone. They show that the same hydrologic and geochemical processes occurred as were reported by Hughes *et al.* (1971) for sites below the top of the zone of saturation. Also, there are reports of rapid movement of contaminants in the unsaturated zone, which cannot be explained as vapor transport. Rapid fluid movement due to capillary forces or gradients in the unsaturated zone must be occurring. Contaminant transport velocities may be many times greater (perhaps up to several orders of magnitude) than the saturated flow velocity (Cartwright, 1982). The following may be an important factor in this regard. Consider the transport of contaminants in saturated porous media; since the effective porosity term appears in the denominator of the Darcy equation, the smaller the effective porosity the faster the transport. While there is not a great deal of information about the effective porosities of fine-grained sediments, there is general consensus that it is a small percentage of the total porosity. As these sediments become unsaturated they lose only a small percentage of their water, even at fairly high tensions. The water lost is essentially equal to the effective porosity. Thus, as the sediments lose moisture, the remaining effective porosity must become increasingly small. If an analogy to saturation can be made, the rate of contaminant transport may increase significantly, perhaps by an order of magnitude. (The whole problem is far more complex than this simple explanation; obviously much research needs to be undertaken in this area.)

Site Size

In recent years there has been a trend from numerous, widely dispersed, small disposal sites to fewer and larger sites (Clark, 1975; Garland and Mosher, 1975). It seems that this strategy should be used with some caution for several reasons. The attenuation capacity of any geologic materials (its capacity to remove contaminants from the water) has a limit, which if exceeded by the volume of leachate that enters the material will allow contaminants to pass through the material almost unretarded. Unfortunately, we do not know enough about the attenuation capacities of geologic materials for most leachate constituents, so we cannot clearly define this limit. Tables 4.2 and 4.3 give the mobility and relative hazard of a few common leachate constituents. Larger landfills are more likely than smaller sites to exceed this limit; therefore, smaller, more widely dispersed sites may be less dangerous to the environment.

Wastes should be segregated where possible. This may be possible to accomplish by designating sites for particular types of waste disposal. Segregation of wastes allows for better prediction of attenuation characteristics of the geologic material using geochemically similar waste materials in an aqueous solution. This is a simpler procedure than predicting attenuation characteristics for mixed wastes. Segregation also prevents interaction among incompatible wastes. Chemical reactions between some wastes may enhance the mobility of certain toxic constituents. For example, the mobility of most heavy metals is directly related to the pH of the solution [generally, the

TABLE 4.2 Ranking of Chemical Constituents in Municipal Leachate According to Their Relative Mobility through Clay Mineral Columns by Mean Attenuation Number (ATN)[a]

Chemical Constituent	Mean Attenuation Number	Qualitative Grouping
Pb	99.8	
Zn	97.2	
Cd	97.0	High
Hg	96.8	
Fe	58.4	
Si	54.7	
K	38.2	Moderate
NH$_4$	37.1	
Mg	29.3	
COD	21.3	
Na	15.4	Low
Cl	10.7	
B	−11.8	Negative
Mn	−95.4	(elution)
Ca	−656.7	

[a] The negative ATN indicates greater concentration emerging from the columns than in the influent leachate, probably the result of ion exchange.

TABLE 4.3 Increase in Salinity of an Aquifer or Small Stream from Landfill Leachate[a]

Hydraulic Conductivity of Liner (cm/sec)	Gradient (cm/cm)	Increase in Aquifer Salinity (ppm)	Increase in Stream Salinity (ppm)
1×10^{-8}	1/1	0.8	0.002
1×10^{-6}	1/10	7.7	0.02
1×10^{-4}	1/100	77.0	0.2
1×10^{-2}	1/1000	769.0	2.0

[a]The salinity of the leachate, using the following assumptions, is low, typical of 20-yr-old sites, not "fresh" refuse: (1) hydraulic conductivity of the aquifer is 1×10^{-2} cm/sec, and its gradient is 1/1000 cm/cm; (2) there is 10^4 m^2 of refuse; (3) aquifer is 30 m thick; (4) leachate salinity is 2000 ppm (Hughes et al., 1971); and (5) stream discharge is 1 m^3/sec.

more acid the solution, the more mobile the heavy metals (Griffin et al., 1976, 1977)], and organic toxicants such as PCBs, which are nearly immobile in aqueous solution, become highly mobile in organic solvents such as carbon tetrachloride (Griffin and Chou, 1981). The present practice of segregating wastes into acids, bases, and organics is woefully inadequate.

The nature and rate of degradation of wastes must also be considered; the waste may change, by some natural process, from its present form to a less complex chemical compound and less noxious form. Categorization into degradable and non-degradable wastes is desirable for all types of wastes because a time factor is added to geologic and geochemical considerations. The decay/decomposition process may result from radioactive decay, organic decomposition, or other processes. Wastes that require a long decay/decomposition period (thousands of years) probably should, from a practical hydrogeologic point of view, be considered nondegradable. These wastes must be diluted to bring the levels of contaminants to acceptable levels (Table 4.4).

Water Balance

The proper balance between water entering and leaving the disposal sites is critical. Wastes are buried in trenches dug in natural clay materials or in trenches having artificial or clay liners of low hydraulic conductivity that will contain the wastes and thereby protect groundwater resources. This approach can create problems in humid climates where the amount of water infiltrating naturally from the surface is greater than the amount leaving the excavation through the surrounding natural material or liner. When this excess infiltration occurs, the disposal trench fills with leachate and overflows, spilling out the sides as springs. This phenomenon is known as the bathtub effect.

The bathtub effect is partly attributable to the fact that most wastes have much higher hydraulic conductivities than the natural material into which they are placed; they also have very different unsaturated soil-moisture characteristics. The hydraulic conductivity of some wastes can be reduced by compaction. Municipal landfill wastes are crushed by heavy equip-

TABLE 4.4 Chemical Constituents in Leachate from a Landfill in Du Page County, Illinois, Ranged by Pollution Hazard Index[a]

Chemical Constituent	Effective Concentration Drinking Water Standard	Toxicity Index	Mobility Index	Hazard Index
NH$_4$	862/0.5	1724.0	62.9	108,440.0
B	(29.9 + 3.5)/1.0	33.4	111.8	3734.0
COD	1340/50	26.8	78.7	2109.0
Hg	0.87/0.002	435.0	3.2	1392.0
Cl	3484/250	13.9	89.3	1241.0
Ca	(46.8 + 307.3)/250[b]	1.42	756.7	1072.0
Cd	1.95/0.01	195.0	3.0	585.0
Fe	4.2/0.3	14.0	41.6	582.0
Na	748/270	2.77	84.6	234.0
Mn	(0.02 + 0.02)/0.05	0.78	195.4	153.0
K	501/250	2.00	61.8	123.0
Mg	233/250	0.93	70.7	65.7
Pb	4.46/0.05	89.2	0.2	17.8
Zn	18.8/5.0	3.76	2.8	10.5
Si	14.9/250	0.06	45.3	2.7

[a]See Griffin et al. (1976) for the definition and derivation of each term.
[b]Actual value not established by EPA; therefore assumed to be the same as chloride.

ment or are processed and compacted with soils from the site to achieve greater and lesser hydraulic conductivity, respectively. If a similar procedure could be followed with toxic waste, fewer problems with the bathtub effect might occur; however, many wastes may be too dangerous to handle in this manner, and different engineering techniques may have to be used to achieve similar results.

The bathtub effect occurs primarily because more moisture enters the landfill area than would infiltrate under normal, undisturbed conditions. Trench covers are generally much more permeable than the natural material or liners below the waste, and both cover and liner play an important role in controlling moisture movement through the waste.

Trench Covers

Trench covers, which are critical to minimizing moisture movement through the waste, were almost ignored until a few years ago, although careful attention has been given to landfill liners for some time. The assumption was that trench covers could be constructed to achieve a desired low hydraulic conductivity and to limit infiltration for the required period of containment or until stabilization of the wastes. However, costly, long-term programs are required to maintain most trench covers. The covers must withstand attack by vegetation, weather (freeze/thaw, wet/dry cycles), erosion, and strain caused by consolidation within the trench. Wastes buried in round barrels are especially hard to deal with since it is very difficult to backfill completely between round barrels, and the voids left eventually cause problems. Trench covers should be designed to utilize hydrogeologic concepts of saturated and unsaturated flow systems and to allow for unexpected consolidation. Research is now under way to design and construct a cover that will control and divert infiltration and will not lose its integrity under moderate compaction of the wastes (see Herzog *et al.* (1981) for a review of the problem). Properly buried and covered, the wastes would be unaffected by surface effects and could meet the containment requirements with minimal monitoring and maintenance.

Trench Liners

Assuming that we can construct a trench cover to match the liner, the question arises as to which type of plastic membrane or clay should be used and, if clay is used, what type clay it should be. (Clay is the name of a large group of minerals all having, among other common characteristics, extremely small, plate-like crystals.) Clay liners can be compacted so that their hydraulic conductivities are very low; plastic membranes can have even lower hydraulic conductivities. Membranes are currently in vogue and are being used in liners and covers; however, little information seems to be available on the longevity of the membranes—even though we are considering the isolation of the waste for perhaps hundreds of years. Some concern has been expressed as to whether these membranes can withstand attack by the array of chemicals buried—especially the organic solvents.

Because of these concerns, clay liners have for many years

been considered best suited for use in burial of wastes; the expandable and chemically very active montmorillonites were usually considered the best material for liners. This type of clay was known to be subject to attack by acids, however, and recent research has shown that some organic liquids can cause cracking in the clay. Other types of clays, even though they provide less attenuation and cannot be compacted to as low a permeability as the montmorillonites, may be more stable. Also burying the wastes in a solid rather than a liquid form might solve this problem. Water leachates of the various chemicals probably would not have nearly so destructive an effect on the clay liners as would "pure" liquid chemicals.

Many of these questions could be solved if expertise from the clay and chemical industry would be brought to bear on them. I still favor the use of some mixture of natural earth materials that allow very slow leakage of leachate from the site and provide attenuation of many of the leachate constituents.

Many landfills—especially the hazardous-waste sites—now have leachate collection systems designed such that the leachate can be intercepted and removed if the cover leaks. This trend to engineered sites with leachate collection systems seems to be a temporary measure, particularly when used for slowly degradable or nondegradable wastes; the leachate collected will have to be disposed of at a final disposal site, perhaps at great expense. Such engineered sites may be suitable for the disposal of degradable wastes where isolation of wastes from the environment is not necessary for long periods of time. Engineered sites may be used to reduce the volume of wastes that must be transferred for final disposal. Treatment to destroy the hazardous leachate components may be difficult, and processing the leachate in a standard waste-treatment plant may only dilute the hazardous substances, possibly causing the sludge from the treatment plant to become hazardous. The idea of collecting leachate from one site and redisposing of it elsewhere resembles "perpetual motion" and can only cause increased difficulties later.

In addition, many of the designs that I have seen for collecting leachate do not correctly apply the basic principles of soil physics (the study of the movement of water in partly saturated soils and rocks). Many collection systems would allow leachate to bypass the collection system if the soil were not saturated and would only intercept leachate when a massive failure of the cover occurs. The collection system thus provides a false sense of security.

MONITORING

The extent of groundwater contamination can sometimes be determined through a groundwater-monitoring program. Reliance on regional groundwater-quality-monitoring programs to identify the contamination problems will not likely be successful since the density of such monitoring would have to be so fine as to be prohibitively expensive. The occurrence of a contaminated well in a regional monitoring network indicates that either (1) the well is located at a point not representative of regional water quality (i.e., an isolated contaminated point in the aquifer, which is not representative of water quality in

the aquifer) or (2) water-quality deterioration in the aquifer is so extensive that it probably is too late for any reasonable action.

The detection of groundwater contamination is a process by which it is determined that the groundwater quality has been altered by the activities of man. Groundwater monitoring is a process by which the extent of contamination is evaluated and the necessity of remedial action is determined. Further, monitoring should provide information as to what type of action, if any, is feasible. As a matter of practicality, detection and monitoring form a continuum and cannot be separated. Detection of groundwater contamination can be approached by systematically searching for sources of contamination and generating new data, by reviewing all existing data and information sources, or by chance encounters. Unfortunately, the last method is the most common.

The hydrogeologic monitoring conducted at waste-disposal sites should address the purpose of monitoring as well as the geology of the site to be monitored. This is seldom done, and thus much of the monitoring that is done may have little technical merit. Thought must be given to the purpose for the monitoring. This purpose may be (a) to verify predictions of contaminant migration; (b) to detect contaminants in drinking-water supplies and thus protect public health; (c) to activate a contingency plan, such as a program for leachate collection; (d) to protect the operator; or (e) a cosmetic procedure to reassure the public. Each of these purposes will require a somewhat different array of monitoring points and a somewhat different sampling program. A proper monitoring system is impossible to design without a specific purpose, or purposes, in mind.

The position of the monitoring points in the contaminant flow path must be determined. To do this the contaminant flow path must be clearly defined in three dimensions. Monitoring points placed in particular parts of the contaminant plume at known distances downgradient from the landfill can be used to estimate contaminant attenuation versus distance and time. This is necessary to measure the highest level of contamination, to judge the effectiveness of the site design, or to predict the future effects of contaminant migration from the site.

Monitoring programs should always be associated with contingency plans. A program designed to detect a potential contamination problem must be accompanied by a program to deal with that problem if it becomes apparent. Contingency plans may, at the one extreme, consist merely of abandoning a water well and, at the other extreme, complete collection and treatment of all contaminants produced by the waste-disposal site. Most contingency plans should require the monitoring program to verify predictions of expected contaminant levels at selected points in the flow system at particular times and should require that critical contaminant levels be specified that require a response. A measure of our understanding of hydrogeologic and geochemical systems associated with a disposal site is the degree to which we can predict the response of those systems to the waste.

Monitoring Methodology

A monitoring methodology is an organized approach to evaluating groundwater quality and specific groundwater contam-

ination problems, thus providing a framework for the planning and development of a technological step necessary to arrive at valid conclusions. Several methodologies exist at the site-specific level, while monitoring "strategies" are being developed at the national and state levels. This discussion follows that of Naymik (1982).

A number of proposed methodologies for monitoring groundwater currently exist. No one particular methodology is the best. While some are quite general, most are tailored to a specific site, because of the differences in goals for the monitoring programs. At the national and state levels, strategies are being developed that will be very general because of the large variation in groundwater problems. At particular sites, methodologies become very specific.

At the national and state levels the word *strategy* is normally used, rather than *methodology*, to describe the framework for planning monitoring programs. A strategy is a general approach that is more of an administrative matter, whereas a methodology is more specific and technological in nature. National and state strategies have not, as yet, been completed. At present, they are being developed within the guidelines of federal directives.

Todd et al. (1976) and Tinlin (1981) suggested methodologies consisting of a general framework for an approach to a site-specific monitoring program (Table 4.5). They must be modified according to the specific situation, such as contamination source, hydrogeologic situation, and political considerations. Persons involved in a monitoring program will be required to exercise professional judgment in order to apply these or any other methodology to a specific site.

Verification of Contamination

Any report of groundwater contamination will have to be verified by sampling and analysis. Water samples have to be drawn from springs or wells. To date, there have been no sampling protocols established for springs, and none may be appropriate. Preservation of all samples will be required using the protocol established for well waters. In addition to normal careful procedures for handling samples to assure correct data, legal chain-of-custody procedures are often called for in such circumstances.

According to Gibb et al. (1981), collecting "representative" water samples from monitoring wells is not a straightforward or easily accomplished task. Each well and surrounding environment has its own individual hydrologic and chemical character. The selection of the type of sampling or pumping device; sample preparation, preservation, and storage; and sampling procedure must be tailored to the size and accessibility of the individual well, its hydrologic and chemical character, the chemical constituents of interest, the time of year, and the purpose for monitoring.

The collection of representative samples was recognized early as a problem in sampling monitoring wells at waste-disposal sites, and several investigators have attempted to establish sampling routines. Hughes et al. (1968) noted the need for flushing monitoring wells and recommended that two well volumes be pumped. (A well volume constitutes the initial volume of water

1ajor Sources and Causes of Groundwater Pollution and Methods of Waste Disposal[a]

	Category			Common Method of Disposal						
	Point	Line	Diffuse	Percolation Pond	Surface Spreading and Irrigation	Seepage Pits and Trenches	Dry Stream Beds	Landfills	Disposal Wells	Injection Wells
∋	x	x		NA[b]	NA	NA	NA	NA	NA	NA
nt	x	x	x	x	x		x		x	
∋	x		x		x	x		x		
	x	x	x	x	x		x		x	
	x				x			x		
rs		x		x						
ation										
ʒ										
)		x		x						
		x		x						
nts		x		x						
l										
		x		x						
;										
d										
	x		x	x	x	x		x		
	x			NA	NA	NA	NA	NA	NA	NA
⁚	x		x	x					x	
's	x			x					x	x
	x		x	x	x		x		x	
)wn	x			x					x	
	x			NA	NA	NA	NA	NA	NA	NA
ent										
nt	x			x				x	x	
s	x			x					x	x
leaks	x	x		NA	NA	NA	NA	NA	NA	NA
	x	x	x	x	x	x	x			x
s	x			x					x	x
	x	x	x	x			x	x	x	x
ɔn										
∋ water	x	x		NA	NA	NA	NA	NA	NA	NA
and										
		x		NA	x	x		x		
icing		x		NA	NA	NA	NA	NA	NA	NA
rusion			x	NA	NA	NA	NA	NA	NA	NA

al. (1976).
cable.

ising prior to pumping.) He also recommends, as d Rovers (1975), that wells installed in materials ulic conductivity be pumped dry and allowed to re sampling. Mooij and Rovers (1975) also rec- umping five well volumes, and Fenn et al. (1977) d three to five well volumes before sampling. al. (1977) demonstrated changes in Pb, Fe, Zn,

Cd, Cu, and Cr concentration in samples from an industrial waste site with the number of well volumes pumped.

Pumping methods or mechanisms also have been shown to affect the quality of groundwater samples. Most operating water wells are sampled using the pumping system in place in the well. The bailer has been used to sample monitoring wells, and Hughes et al. (1968) and Mooij and Rovers (1975) suggested

that this was the preferred method of sampling. Air or gas lifts have also long been used for sampling monitoring wells (Hughes et al., 1968; Trescott and Pinder, 1970; Sommerfeldt and Campbell, 1975). However, several groups have cautioned against the exposure of groundwater to the air during sampling as it may cause chemical changes, especially in pH, alkalinity, and iron (Wood, 1970; Wallich (1977). In recent years small-diameter downhole pumps have been developed that may solve many of the problems encountered with other pumping mechanisms.

CONCLUSIONS

The problems discussed in this paper do not have easy answers. In most cases we must make trade-offs between various competing solutions. One thing is certain: there will always be a need for land disposal of waste. Even if "complete" recycling were to occur, the sludges and residue from recycling plants and furnaces would then have to be disposed of. I believe that land burial of waste is a safe method to use with most wastes, provided that the disposal site is properly located and engineered, using the best technology available and a good measure of common sense. Each land-disposal site must be considered as unique and the disposal operation engineered specifically for that site.

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Deep Burial of Toxic Wastes

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ABSTRACT

Deep burial of toxic wastes provides several advantages over disposal in surface structures or by shallow burial. The primary advantage of deep burial is the high degree of physical isolation that it provides. Some of the hydrogeologic advantages of deep burial are (1) increase in length of flow path of contaminants that may become dissolved in groundwater; (2) increased protection of waste against weathering and erosion; (3) for some wastes and waste containers, elimination of free oxygen that may mobilize certain constituents; and (4) for plutonic rocks and to some extent all rocks, reduction of permeability with depth. Primary disadvantage of deep burial is the high cost of exploration, development, and monitoring of deep disposal systems.

Reduction of permeability with depth in metamorphic and plutonic igneous rocks is well defined to depths of about 300 m. Further reduction of permeability with depth probably takes place but is difficult to quantify using present data. Most of the reduction in permeability with depth in sedimentary rocks is within the upper 100 m. The reduction of permeability is generally at least three orders of magnitude from near the land surface to depths of 100 m for all types of indurated rocks. Based on hydrogeologic criteria alone, many different rock types should provide safe waste repositories at depths greater than 100 m.

Deep repositories in most locations will eventually fill with water. However, if zones of significant groundwater circulation are either avoided or grouted, repositories at depths of more than 300 m in granitic rocks should take several hundred years to fill with groundwater once they are closed. In a well-placed repository, several thousand years may be needed to accomplish a simple piston-flow displacement of all water in the flooded repository. Even this length of isolation may not allow enough time for the degradation of all wastes to take place, but a long isolation time will most commonly mean a slow release of mobile contaminants into the biosphere, which, in turn, suggests that dilution will be more effective than in the case of a fast release of contaminants from shallow burial sites.

INTRODUCTION

Humans have produced toxic wastes since before recorded history. At least four factors, however, have made the problem of toxic waste disposal far more acute within the past 100 yr than at any previous period. First, and most obvious, is the human population explosion and the fact that most of the additional people have accumulated in urban areas. The second is the development of numerous industrial processes that have toxic wastes as a by-product. The third is the development of the ability to concentrate and produce radionuclides. The fourth is the public awareness of the toxic waste problem, which has,

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paradoxically, made the solution both possible and at the same time more difficult.

Public awareness has forced the formation of the legal framework to control the wastes and has stimulated funding to help solve the technical problems of disposal. However, concern about the hazards has given rise to an almost universal resistance to the creation of repositories for hazardous wastes. Commonly, the same groups that have lobbied for the formation of strict laws that force the creation of special waste repositories join forces with local citizens to prevent the actual construction of repositories at any specific site. Partly as a consequence of this resistance, in some regions the actual disposal of waste is so difficult, owing to great distances to approved disposal sites or to excessive disposal costs, that illegal and highly dangerous dumping of wastes has been practiced.

Even though the location, authorization, and preparation of disposal sites for hazardous wastes have been slow partly owing to the public's "not in my backyard" reaction, the additional time made available due to the delay is being used beneficially. Analytical methods are being developed that will allow a more precise characterization of hazardous wastes; alternative methods of packaging, transportation, and disposal are being studied; legal and administrative procedures are being perfected; and time for a balanced public education program is available.

The present production of hazardous wastes in the United States is measured in several tens of millions of cubic meters per year (United States Congress, 1979). The exact amount varies according to the classification system used. Unfortunately, only a small fraction of this waste is currently treated or disposed of in a satisfactory manner (Council on Environmental Quality, 1981). Compaction, evaporation, and chemical treatment of the waste may eventually transform much of the waste to an innocuous form and reduce the volume of the remaining hazardous material to only a few million cubic meters per year, which will still require disposal in highly engineered structures. Even if this optimistic goal is achieved, the disposal of this volume of material still requires a major national effort. Because the principal mechanism for escape of hazardous waste to the biosphere is through groundwater flow, involvement of the geologic profession in this effort is essential for the proper solution of the problem (NRC Committee on the Geological Aspects of Industrial Waste Disposal, 1982)

Wastes can be hazardous because of the presence of (a) toxic chemicals, (b) chemicals that are initially innocuous but turn toxic on degradation or reaction with other chemicals, (c) explosive or combustible materials, (d) sharp objects that will cut or puncture, (e) large objects that will collapse or tumble, (f) radioactivity, and (g) pathogenic organisms. Unless noted otherwise, the remainder of this chapter will be confined to a discussion of only the more stable toxic chemicals and materials contaminated with radionuclides having half-lives in excess of several decades. Although the broad topic of the disposal of radioactive waste is not treated in detail, the similarity of the programs of disposing of transuranic and some low-level radioactive material to problems of hazardous chemical wastes makes it convenient to combine all hazardous chemical and radioactive wastes in the discussion.

METHODS OF DISPOSAL

A large number of methods of disposing of toxic wastes exist. Large concrete mausoleums, slurry injection in deep wells, trenches in desert regions, and repositories mined in bedrock are some of the options of disposal. From a purely hydrogeologic standpoint, trench burial in dry permafrost, which would receive prefrozen wastes, would be the most acceptable method of disposal. The delicate nature of the Arctic environment, the physical difficulties of operating in such a harsh climate, and its remoteness from points of origin of the waste, however, suggest that extensive use will not be made of dry permafrost for the disposal of hazardous wastes. The eventual choice of a method and geographic location will be a function of waste form, level of hazard present, duration of the hazardous characteristics, availability of a proper natural setting, and complex economic and legal factors. Although a number of disposal methods will be used eventually, this chapter will discuss only deep repositories mined in consolidated rocks. For this chapter, "deep burial" will be considered to start at depths of 100 m. The existence of alternative disposal methods is assumed, so that only highly compacted wastes that will remain hazardous for thousands of years are considered for deep burial.

Actual burial of waste will be assumed to be in mined cavities within rocks of low porosity and permeability. Although excavation and placement of wastes may be accomplished by remotely controlled methods, all shafts and cavities will be large enough for human entry for various purposes including testing, inspection, and monitoring. Deep burial will require considerable investment of effort and money for site preparation and sinking of shafts; consequently, large volumes of waste, perhaps as much as 10^5 m^3 of radioactive waste or 10^6 m^3 of chemical waste, would probably need to be buried in a single repository in order to justify the overall investment in such an undertaking. Even with multilevel placement of drifts, the excavation alone would most likely underlie at least 100 hectares.

The concept of multibarriers to the migration of wastes, which has been discussed widely in connection with radioactive wastes (U.S. Department of Energy, 1979; Davis, 1982; NRC Board on Radioactive Waste Management, 1983), should be applied to all repositories. An attempt should be made to convert the waste into a chemically inert, nonpermeable form. The waste should then be packaged in strong, resistant containers to facilitate handling and to retard contact with groundwater after burial. Drifts and shafts should be backfilled with material having a low permeability combined with a high capacity to sorb water-transported contaminants. The host rock should be grouted along fractures to reduce further the already low natural permeability. The host rock should be chosen for its mechanical stability, for its low permeability, and for its uniformity of mechanical and hydrogeologic properties. The repository should be placed in an area that would favor a long flow path of the groundwater prior to the groundwater's emerging at the surface or into a large body of water such as the ocean (Bredehoeft and Maini, 1981). This placement would allow time for chemical and radioactive decay as well as dilution of the contaminants in the groundwater. Thus, the multiple barriers

would be waste form, packaging material, backfill, engineering modification of host rock, host rock, and, finally, the long migration path prior to the emergence of contaminants at the land surface.

ADVANTAGES AND DISADVANTAGES OF DEEP BURIAL

Deep burial of toxic wastes has several advantages over shallow burial or surface storage systems. One of the most important advantages is that contaminants that may become dissolved in groundwater will not migrate directly to the land surface. The increased length of the groundwater flow path will allow time for the decay of radionuclides, the decomposition of unstable chemical compounds, and the dilution of toxic materials by dispersion. Deep burial will commonly place wastes in zones near or adjacent to natural saline or brackish water, which, in contrast with surface water, has little or no practical value and, if contaminated, would not represent a large loss. Deep burial will also afford protection against the possibility that the hazardous materials will be exposed at the surface through slow processes of erosion. Finally, and perhaps most important, deep burial will make human intrusion less likely.

The depth of burial that may be chosen is related generally to rock permeability so that the deeper the burial, the lower the permeability. As will be shown, however, the reduction of permeability is small beyond depths of about 300 m. The reduction in the first 50 m, in contrast, is most commonly at least one order of magnitude.

Generally, pH, salinity, and alkalinity of natural water increase with depth, but concentrations of nitrate and dissolved oxygen decrease (Davis, 1981). For some wastes, the chemical characteristics of deep groundwater may have some advantages over the chemical characteristics of shallow groundwater. For example, many of the transuranic elements will be less mobile in the deeper groundwater, where chemically reducing conditions prevail.

The most serious disadvantage of deep burial is economic. Deep repositories will be expensive to construct; they will be difficult to monitor; and if errors are made or unexpected flaws in the repository are uncovered, the removal of the waste in order to place it in a better location will be costly.

Estimates of costs (in 1982 dollars) of constructing deep repositories for high-level nuclear waste generally range from about $1.5 billion to $1.7 billion (Waddell et al., 1982). Such repositories would be designed to receive about 7.0×10^4 metric tons of high-level waste in about 1.25×10^5 containers of various types having a total volume of about 1.1×10^5 m^3. The cost of the repository includes site acquisition, site improvements, receiving facilities, excavation of underground workings, and ventilation systems. It does not include operation costs nor waste preparation facilities. If one assumes equal costs for a mined repository for hazardous chemical wastes, then it becomes clear that such a structure can be justified only for the most hazardous wastes. For packages of nuclear waste, the cost will be in excess of $10,000 per m^3 of packaged waste. If operating and processing costs are added, the total costs of

disposal will be more than $30,000 per m^3 of waste (Waddell et al., 1982). Similar cost estimates are not available for a hypothetical deep repository constructed to receive only chemical wastes. However, the costs should be considerably less because the heat dissipation problem of high-level waste, which prevents close packing of the waste, will not be present. Therefore, the volume of chemical waste accommodated should be much larger than for high-level wastes, perhaps by an order of magnitude. A guess of possible costs might range from $5000 to $10,000 per m^3 for chemical wastes, which would include construction of the repository and operating costs. Even with extra close packing of waste containers and relaxed problems of waste handling, it is hard to visualize a total cost of less than $1000 per m^3 (or $1 per liter) for deep burial with isolation requirements similar to that of nuclear waste.

Costs of burial in shallower mined cavities would be much less. Estimates of costs in mined space in salt together with conventional facilities to handle packages of low-level radioactive waste suggest costs of about $100 (1978 dollars) per m^3 for a volume of 1.5×10 m^3 of waste to be placed in the repository each year (Wacks, 1979).

In conclusion, the cost of waste disposal will probably range from $100 to $200 per m^3 for not-so-hazardous materials to a few thousand dollars per cubic meter for very hazardous chemical wastes and as much as several tens of thousands of dollars for high-level radioactive waste. Exact costs are most sensitive to variations in the density of waste placement in the subsurface; requirements for special containers and packaging procedures; and methods of transporting, storing, and handling the materials prior to subsurface disposal (Clark and Cole, 1982). Total costs for repositories for high-level wastes are not highly sensitive to variations of depth and geology, which help determine the costs of the excavation of subsurface space, because processing, packaging, and handling together comprise the largest part of the total cost.

A HYPOTHETICAL REPOSITORY

Deep geologic repositories of various designs have been proposed for the disposal of radioactive wastes (St. John, 1982). If the economic factors become favorable, similar repositories will undoubtedly be proposed also for highly toxic chemical wastes. From the standpoint of scientific factors, no general reason exists that properly packaged chemical wastes, particularly if they are in solid form, could not be placed in the same repository with transuranic and low-level radioactive wastes. In the United States, however, institutional arrangements for the supervision and control of hazardous chemical wastes are generally separated from radioactive wastes. Construction of a joint-use repository would seem to be unlikely for the next few decades. Consequently, the hypothetical repository described will be assumed to be only for the purpose of receiving toxic chemical wastes.

The selection of a repository site will undoubtedly follow many of the criteria developed for locating sites for nuclear waste (Bredehoeft et al., 1978; NRC Panel on Geologic Site

Criteria, 1978; U.S. Department of Energy, 1979, 1983). The following are general criteria as adapted from St. John (1982):

(a) Site geometry	Adequate depth, thickness, and lateral extent of host rock
(b) Host-rock properties	Low permeability and mechanical strength sufficient to allow for stable excavations; chemical composition of waste will not react adversely with rock
(c) Hydrology	Low groundwater velocities; long distance from points of potential contamination to points of use of potable groundwater
(d) Tectonic stability	Uplift or subsidence at rates low enough not to be a threat to the longer-term stability of the site
(e) Seismic activity and faulting	Located away from active faults that would threaten operational safety or long-term containment; not located in areas of major historical earthquakes
(f) Volcanism	Site would avoid areas of Quaternary volcanism
(g) Natural resources	As far as practical, located away from areas that invite exploration for natural resources

Similar criteria for the siting of near-surface disposal of hazardous wastes have been proposed by Longmire *et al.* (1981). Redistribution of toxic material by erosion, human intrusion, deep plant roots, or burrowing animals is, however, potentially more troublesome in near-surface disposal than in deeper burial in bedrock. An attractive compromise between shallow burial and deep repositories has been proposed by Winograd (1974, 1981) for radioactive waste. He has pointed out that the nonsaturated parts of alluvial fans in the deserts of the Southwest are commonly more than 50 m thick and provide an environment generally free from percolating water. Moreover, many of the fans are either not being eroded or are still growing so that future uncovering by erosion would not take place for many thousands of years.

A large number of geologic settings are being considered for repositories for radioactive wastes. Many of these will undoubtedly meet the requirements. A discussion of the various strengths and weaknesses of all of these geologic settings is beyond the scope of the present review. I have chosen only one general type of setting for a more detailed discussion of a potential repository for toxic chemical wastes. This setting is within metamorphic and plutonic igneous rocks. This setting is considered a likely candidate because (1) large regions of the world have vast areas underlain by these rocks at shallow depths; (2) mining of these rocks is rapid and yields vaults that are stable for long periods; (3) areas having deposits of economic interest are identified and avoided more easily than in sedimentary rocks that may contain gas and oil; (4) unplanned human intrusion into the repository is less likely than in softer rocks; (5) the rocks generally have a low permeability and, where fractures are present, grouting can be completed efficiently; and (6) uncovering the contents of the repository by

erosion would generally be slower than with most other rocks, given equivalent geographic locations.

Conceptually, a repository will start at a depth of about 300 m and will be covered by at least 200 m of bedrock. An aquifer may be near the surface. As pointed out by Bredehoeft and Maini (1981) (Figure 5.1), this aquifer may actually be a favorable feature, particularly if the aquifer discharges groundwater directly into the ocean or a large lake. Groundwater in the aquifer would serve to carry the small amount of escaping toxic material away from the site and would serve as a dilution mechanism, which is described later in this chapter.

A repository shaft starting in metamorphic and igneous rocks at the surface will penetrate weathered material at varying depths (Figure 5.2). Joints and fracture zones tend to be weathered to the greatest depths. The joints and fractures commonly enclose large residual blocks of unweathered rock. Unusual care is needed, therefore, in this transition zone with its highly variable rock conditions to ensure proper sealing of the shaft during closure of the repository.

HYDROGEOLOGIC PROPERTIES OF ROCKS AT DEPTH

General Data from Wells and Test Holes

Most permeability data for igneous plutonic and metamorphic rocks deeper than 100 m come from the interpretation of packer tests in drill holes (Snow, 1968; Lindblon, 1977; Davison, 1981). A small number of aquifer tests using data from flowing or pumping wells in deep bedrock have also been completed (Marine, 1967). For depths of less than 100 m, abundant data from both water wells and exploratory test holes are available (Davis and Turk, 1964; Stewart, 1966; Landers and Turk, 1973; Mundi and Wallace, 1973; Uhl, 1976; Gale, 1982).

The fact that the specific capacity per unit thickness of saturated rock penetrated by a water well decreases rapidly with depth has been noted by hydrogeologists for almost 100 yr. This trend is most marked in shale, limestone, metamorphic rocks, and plutonic igneous rocks. Typical graphs of data from different areas are shown in Figure 5.3. Two possible explanations for these trends exist. First, and most obvious, the permeability decreases with depth. Second, the data may be only an artifact of the way in which water wells are drilled and may only indicate lateral variations of permeability. In other words, where permeable rocks are encountered, drilling stops at a shallow depth and a high near-surface permeability is suggested. In contrast, where rocks of low permeability exist, wells are drilled deeper in search of water and the apparent overall permeability of the rocks is low.

Although the type of bias in the data that I have suggested above may have some effect, it must be small. Davis and Turk (1964) and later investigators (Snow, 1968; Lindblon, 1977; Johnson, 1981) have looked at data obtained during the exploration for dams and tunnels, some of which should have a bias in the opposite direction. Specifically, many deep holes have been drilled in order to search for permeable zones. Hence, data from a large number of drill holes would probably have a
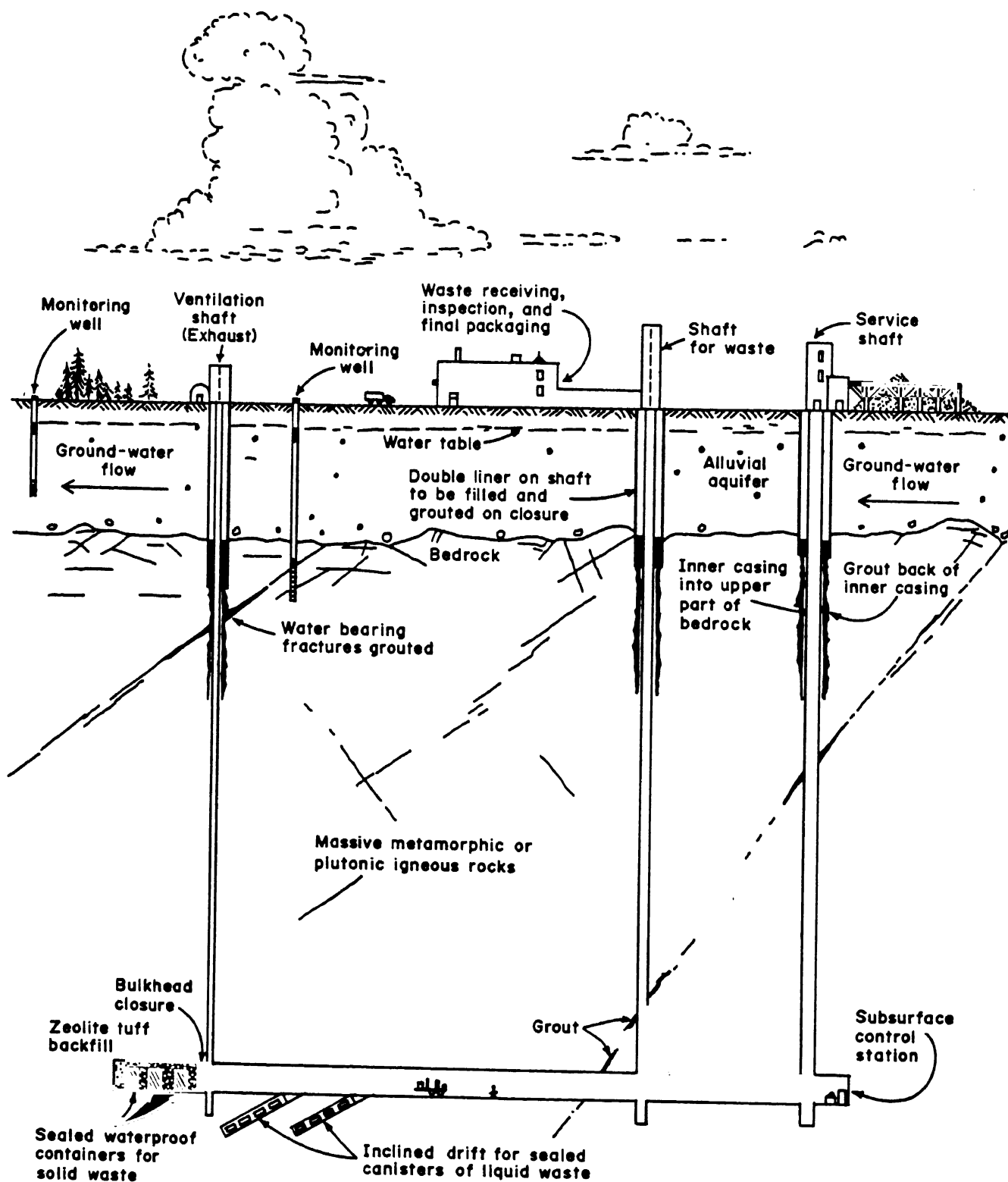
FIGURE 5.1 Type of repository development that may be possible for toxic chemical wastes. Features shown are not to scale, and all shafts and drifts are not shown. Full development would involve one or more levels having a gridlike network of drifts. Mining, placement of waste, and eventual closure would follow a sequence that is not indicated in the figure.
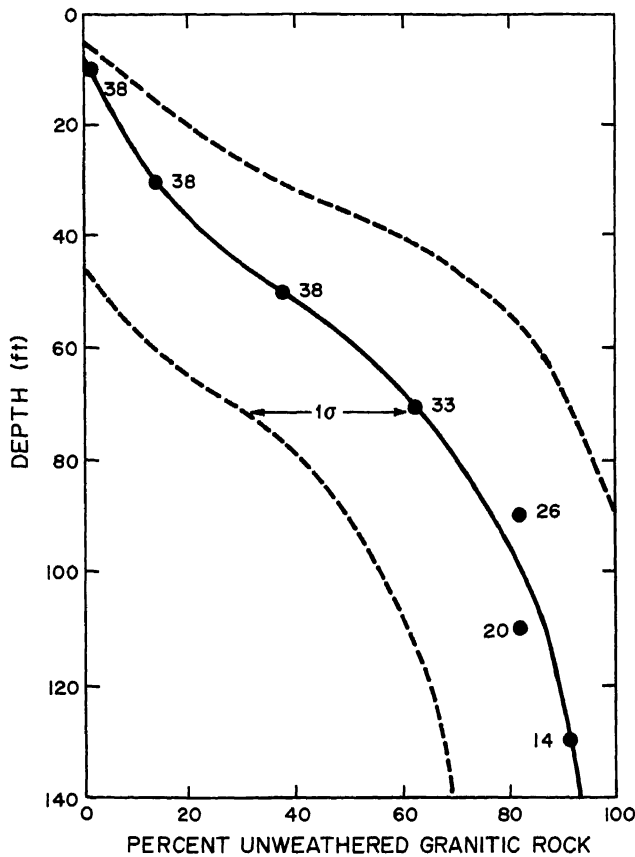
FIGURE 5.2 Percentage of unweathered rock as a function of depth at the Folsom Dam site in California. The total number of drill holes that supplied data for each depth interval is given next to each plotted point. Data are from unpublished reports of the U.S. Army Corps of Engineers and were compiled by Davis (1981).

bias in favor of a greater permeability at depth. However, the location of the dam or tunnel most commonly favors areas of sound rock, so permeabilities of rocks within the area in general would tend to be lower than adjacent areas. The general conclusion is that test-hole data also show a decrease of permeability with depth that is similar to water-well data (Figures 5.4, 5.5, and 5.6). In general, the well-defined decreases in permeability are caused by at least the following five factors (Davis and Turk, 1964):

1. A decrease in the effects of surficial weathering with an increase in depth (Figure 5.2).

2. An increase in distance between joints, particularly sheeting joints, with depth.

3. An increase of lithostatic pressures with depth that tends to close fractures at depth.

4. A decrease with depth of fractures related to mass wasting.

5. A decrease with depth of the effect of topography on those stress patterns that might help contribute to localized rock failure.
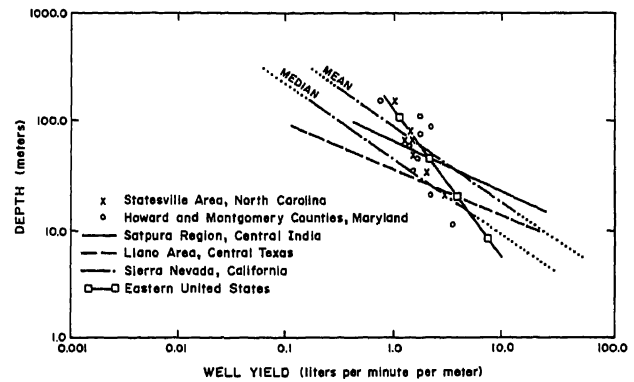
FIGURE 5.3 Depth-yield relationship for water wells in metamorphic and plutonic igneous rocks. With the exception of the one line labeled "median," data used are from mean specific capacities of wells of different depths. Diagram by Johnson (1981).

Even though a large number of mines in consolidated rocks are virtually dry, the fact that many actually produce large amounts of water (Cook, 1982) suggests that those sites where proper conditions exist for geologic isolation of wastes may be difficult to locate. As Cook has pointed out, much of the permeability, which allows an initial inflow to excavated openings, is local and has been caused by strains associated with the mining itself. If this permeability is potentially too large, repository extraction ratios must be kept low. Nevertheless, it should be remembered that most mines from which data are available are in hydrologically anomalous regions where various types of geologic discontinuities should favor natural zones of locally high permeabilities that contain water and would be intercepted by zones of artifically high permeability near the mines. Data on rock permeabilities from mines in general should, therefore, be considered as representing the higher extremes to be expected.
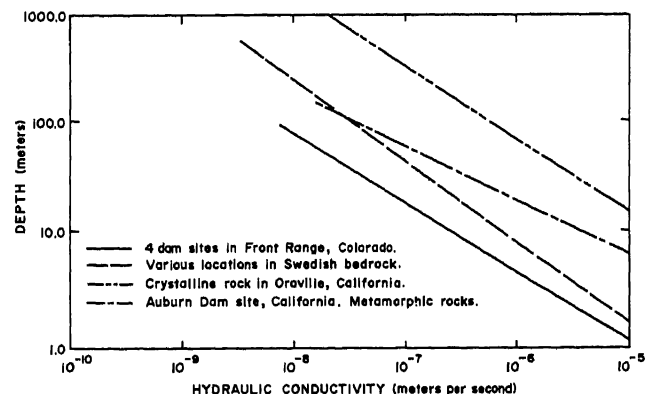
FIGURE 5.4 Results of packer tests in drill holes penetrating metamorphic and plutonic igneous rocks. Trend lines are based on the mean hydrualic conductivities at various depths (Johnson, 1981).
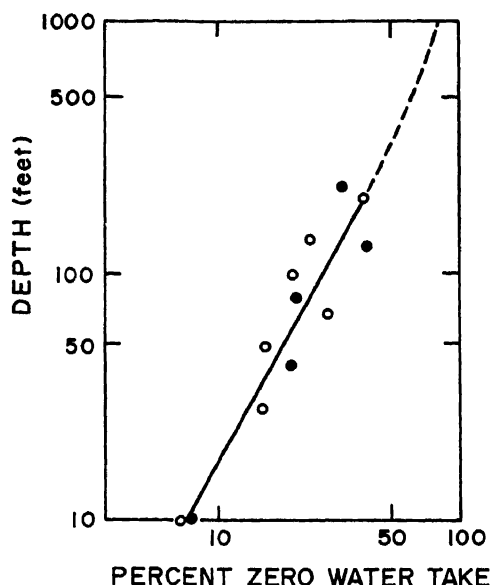
FIGURE 5.5 Diagram showing the increase in nonpermeable zones with depth in metamorphic (open circles) and plutonic igneous rocks (black dots) of the Sierra Nevada, California. Data are from U.S. Bureau of Reclamation drill holes. Individual points represent data from at least 30 packer tests at various depth intervals. The percentage of packer tests that were unable to inject water are plotted for each depth interval (Davis and Turk, 1964).
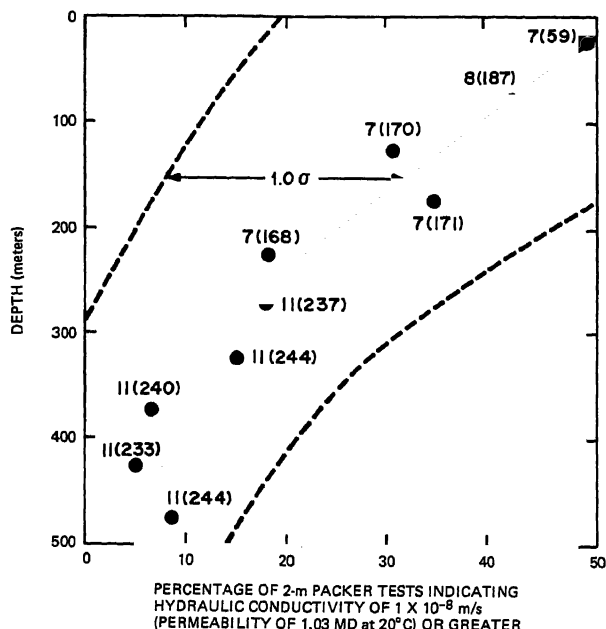
FIGURE 5.6 Diagram showing the reduction in the number of permeable zones with depth in metamorphic and plutonic igneous rocks of Sweden. Percentage values for each 50-m depth interval are plotted. Small numbers indicate the number of test holes in which the packer tests were performed, and the larger number in parentheses gives the total number of packer tests for each depth interval (Davis, 1981).

Many permeable zones encountered in mines and tunnels drain rather rapidly, and little water is produced from these zones after a few days even though the zones may be a long distance beneath the regional water table. This general observation suggests that many permeable fractures in metamorphic and plutonic igneous rocks have a limited extension. This qualitative conclusion is supported by aquifer tests and other tests completed on test holes in metamorphic rocks underlying the Savannah River Plant (Marine, 1981).

Geochemical Evidence

Several aspects of water chemistry suggest that much of the water in the deep subsurface is almost static, and, under natural gradients, the movement of potential contaminants in this water toward the surface would be so slow that it would be negligible. One of the most important aspects of repository design is to ensure that this remains so. The most basic argument for the conclusion that the water is nearly static comes from the high chloride content of almost all deep water. Because significant amounts of chloride do not come from the dissolution of minerals except in obvious cases where evaporites are present, the most important reason for the high chloride content in the water would be either the presence of ancient formation water or the concentration of chlorides through ion filtration. In the case of ancient formation water, if an active circulation system is connected with the land surface, the chloride would have been flushed out long ago by infiltrating surface water that has a chloride concentration from three to four orders of magnitude less than would be present in today's subsurface brines.

In contrast, if subsurface brines are the end product of chloride concentrating by means of ion filtration, water circulation would need to be quite vigorous in order to account for the total mass of chloride present in the aquifer. For example, if a sandstone outcrop, which is also the intake area of an aquifer, is 3 km wide and 1 m of water having 10 mg/L of chloride enters the aquifer each year, then for every 1.0 m along the strike of the aquifer, a total of 3×10^7 mg of chloride enters the subsurface each year. If the same sandstone has a porosity of 20 percent and extends downdip 50 km with an average thickness of 20 m and is saturated with water having 20,000 mg/L of chloride, then a total of 2×10^{12} mg of chloride is present in each 1-m strip perpendicular to the strike. Thus, about 7×10^4 yr would be needed to accumulate this amount of chloride if the ion filtration is 100 percent efficient. The velocity of groundwater needed (750 m/yr) in this example would be very large for a natural system that might also be near a waste repository. The correct interpretation of the origin of the chloride in the groundwater is, therefore, critical to the safety evaluation of the waste-disposal system.

Studies of the quality of water from deep drill holes and mines in metamorphic and plutonic igneous rocks generally show an increase of salinity with depth (Jacks, 1973, 1978; Marine, 1976; Davis, 1981; Frape and Fritz, 1981). In general, water contains less than 1000 mg/L total of dissolved solids at depths of less than 100 m. Concentrations increase to more than 10,000 mg/L as bedrock is penetrated to depths of more than 1000 m. Isotopic composition of the deeper water suggests

that the major dissolved constituents are unrelated to modern surface water and that they probably are not derived from ancient seawater (Fritz and Frape, 1981; Nordstrom *et al.*, 1982). The salinity may be caused by the slow diffusion of small amounts of ions from original metamorphic and magmatic water in micropores in the dense rock into larger fractures that penetrate into the subsurface (Nordstrom *et al.*, 1982). The ability of minor amounts of interstitial brines to increase significantly the salinity of water in fractures has been demonstrated in the Hot Dry Rock Energy Extraction test in New Mexico. Here, water of low salinity was injected into large artificial fractures made within nonpermeable geologically young plutonic rock. The first return water from this injection showed large increases in total dissolved solids as well as a number of key ions. For example, chloride concentrations in one of the injection cycles increased from less than 50 mg/L in the injected water to 1750 mg/L in the initial water circulated back to the surface from the fresh fracture (Smith and Ponder, 1982).

To summarize the chemical evidence, in metamorphic rocks and plutonic igneous rocks the salinity of water in fractures increases with depth. If ion filtration can be discounted as a mechanism for concentrating these dissolved solids, then it is suggested that the chemical composition reflects water within fractures in these rocks, which approaches stagnation at depths of from 300 to 1000 m in most regions. This is, then, a further argument for the safety of deep burial of wastes within these rocks.

PROBLEMS OF EVALUATING THE HYDROLOGIC HAZARDS OF A WASTE REPOSITORY

Flow of groundwater through a waste repository is the most likely natural mechanism for the transportation of hazardous materials from the subsurface into the biosphere. Several questions must be posed concerning this potential source of contamination. These can be generalized as follows:

1. If contamination reaches the surface, where will this take place?
2. What will be the predicted concentrations of these contaminants in the water when it reaches a point of use?
3. What will be the total amount of contaminants to reach the surface?
4. How long will the contaminants take to reach the surface?

Each of these questions will be discussed in a general way in relation to the hypothetical repository.

Trajectory of Contaminants

The trajectory of a contaminated plume of groundwater from the repository will be particularly difficult to predict within a few hundred meters of the repository. After an initial non-steady-state flow, which will be controlled by the repository geometry and construction and may last a few months, the subsequent pseudo-steady-state flow of water will be controlled primarily by major fracture zones in the bedrock. Within the major fractures, flow could be locally almost at right angles to the trajectory of the water, which might be predicted on the basis of regional hydraulic head measurements in the overlying aquifer. The location of the major fractures that form potential conduits is aided by geologic and geophysical methods but probably will never be precise enough to allow an exact definition of the details of groundwater flow in the vicinity of the repository. Once the contaminated water reaches the more permeable upper part of the bedrock and the base of the overlying aquifer, however, it will move downgradient in the same general direction as the bulk of the groundwater in the aquifer. After a few kilometers of migration, transverse dispersion should work the contaminated water into the upper part of the aquifer where it will eventually reach the biosphere through downgradient wells, springs, or diffuse seepage into large bodies of water. The assumed upward diffusion into the aquifer, nevertheless, could be inhibited almost indefinitely if the density of the contaminated water is much larger than normal groundwater and if the aquifer is horizontal with abundant clay lenses, which would have the effect of producing a strongly anisotropic flow in the horizontal direction.

Concentration of Contaminants

No method exists to predict concentrations of contaminants in groundwater passing through a repository because of the uncertainties in the source term. Containers for waste will be built to last as long as practical, and their rate of failure will be unknown. Once the container is breached, the contents will be removed slowly by water. Some rough estimates of the rates of this removal can be made based on the results of laboratory tests. Backfill around containers, however, will be designed to sorb as many of the contaminants as is practical. The rate of migration of contaminants through the irregularly shaped backfill probably can only be bounded in a broad way by generalized calculations.

The usual method of handling the source-term problem of predicting concentrations is to assume some physically reasonable rate of removal of the repository contents and arbitrarily inject this hypothetical amount into a mathematical model of the moving body of groundwater. Sophisticated transport models then are used to predict downgradient migration rates and concentrations. The transport models, unfortunately, lend an air of authenticity that is rarely justified because of the arbitrary assumptions made in the source terms.

The movement and dispersion of contaminants once the groundwater leaves the artificial cavities and enters the surrounding host rock will be very difficult to define in great detail. As the water moves into the regional flow field, nevertheless, useful approximations of contaminant concentrations can be made for any hypothetical source term.

Total Amount of Contaminants that Reach the Surface

A concern for the total amount of contaminants that eventually reach the surface is particularly acute in relation to the burial of radioactive wastes. This concern exists because, for lack of better evidence, adverse health effects from radiation are as-

sumed to be linearly related to the radiation dose received by humans. Thus, even very low levels of radiation widely dispersed in the environment, if extended over a long period of time and if enough people are exposed, may cause the same total number of health effects as would a highly concentrated dose to which only a few people were exposed. One stategy for reducing the total amount of radionuclides reaching the biosphere is, therefore, to increase the time of isolation to allow for radioactive decay.

The problem of isolation of hazardous chemical wastes has not been handled in the same way as radioactive wastes. The long-term stability of many compounds under conditions of burial are poorly understood. Certainly, some complex compounds will break down with time so that isolation renders the wastes less hazardous. Many compounds and elements such as cadmium and arsenic, in contrast, are stable for an infinite period, so that the time of isolation alone will not affect the total amount of contaminants that will eventually reach the surface. The seriousness of the eventual movement of trace amounts of these stable materials to the Earth's surface has not been studied in detail. Can we assume a linear relationship between the hazardous chemical and resultant adverse health effects? Probably not. For example, arsenic, in milligram amounts, is hazardous. However, current evidence suggests that arsenic in nanogram amounts is essential to human health (Mertz, 1981). Thus, simple dilution of wastes containing arsenic could eliminate all adverse health effects from this contaminant. In this example, the total amount of a contaminant reaching the surface is, therefore, of much less importance than the projected maximum concentrations, which would control the dose to individuals.

Travel Time

Estimates of the time that might be taken for a contaminant to be transported by groundwater from a subsurface repository to the land surface should be made for most repositories. In general, the longer the travel time is, the more favorable the site will be; although some hydrogeologic situations certainly exist where additional travel time does not necessarily mitigate potential hazards from toxic chemicals. Additional time in most settings will allow for dilution by molecular diffusion, decay of radiaoctive components, and decomposition of hazardous compounds. Most important, long travel times will help with the public acceptance of a site. Contaminants that might reach the land surface after thousands of years may be of little direct concern to the average citizen.

The calcuation of travel time, unfortunately, is commonly accomplished only by assuming "reasonable" values for a number of critical factors. Using different assumptions, hydrogeologists can calculate travel times for waste from the same repository that may vary from one another by an order of magnitude or more. This is particularly true of irregularly fractured metamorphic and plutonic igneous rocks.

The following equation can be used to calculate the increment of time, Δt, for the average time that a particle of groundwater takes to traverse a given distance, ΔL:

$$\Delta t = \frac{N_e(\Delta L)^2}{K\Delta h}, \qquad (5.1)$$

in which K is a measure of hydraulic conductivity of the rock, Δh is the head drop over the distance ΔL, and N_e is the effective (interconnected) porosity. The value of K can be estimated from field tests, and the values of ΔL and Δh are commonly determined to some extent by known boundary conditions. The value of N_e however, for fractured rocks is rarely determined with accuracy and may easily vary from about 0.5 for weathered rock to 0.05 for highly fractured rock to less than 0.005 for dense, sparsely fractured rock. Calculated travel times would vary in the same way and are more often based on porosity values that are assumed rather than measured.

Chemical variables introduce even greater uncertainties in travel-time estimates than do problems of defining the effective porosities of the rocks. Most chemical species dissolved in water will be sorbed to some extent on the solid matrix of the water-bearing materials. Even though desorption takes place, most chemical species will partition strongly onto the solid matrix. This means that the chemical species that is a potential contaminant will usually travel at only a small fraction of the velocity of the groundwater. Theoretically, the relative velocities of the chemical species and the groundwater can be measured by laboratory experiments. In practice, however, only an order-of-magnitude estimate is commonly possible. The chemical processes involved in the transport phenomena are a complex function of pH, chemistry of the solid surfaces of the rocks, nature of the dissolved species, temperature, water velocity, total volume of water flowing, other dissolved species in the water, and the relative concentrations of those species. These variables must be specified in time and space for the complex natural setting in order to estimate the velocities of contaminant migration. An early error of chemists dealing with this problem was to conduct laboratory experiments with artificially crushed rock and consider only mineralogical properties of the rocks, whereas the thin natural coatings along fractures in the rocks, which would not show up in bulk analyses, will actually be the most important control in the sorption process.

A process similar to sorption in fractured media is that of molecular diffusion into the micropores in the otherwise solid rock. This process is important if the migration of the contaminant is slow, which would allow time for diffusion to take place. Molecular diffusion would, therefore, serve to slow down the velocity of contaminant movement by allowing these contaminants to migrate through the rock as well as through the more open fractures.

FLOW OF GROUNDWATER THROUGH A CLOSED REPOSITORY

Initial Inflow

After the repository is filled with waste and access shafts are sealed, the repository should become saturated with water if it is below the water table. The rate of inflow of groundwater, however, should be quite small, particularly if fractures leaking

significant amounts of water have been grouted during exca-
vation of the repository. The process of saturation may take
from decades to thousands of years, depending on the perme-
ability of the rock and whether gases are easily expelled from
the closed repository and also depending on the depth of the
repository beneath the water table.

Once the repository is saturated, water will move slowly into
the structure and then drift out the downgradient side. If waste
is in an insoluble form or if waste containers are watertight,
the initial water flowing through the repository should not
become contaminated. However, containers in the repository
will ultimately fail, and "insoluble" material will dissolve to
some extent so that water flowing through the repository will
eventually be contaminated. The length of time taken for con-
taminated water to start to move out from the repository after
the repository has become saturated could be in the range of
hundreds to thousands of years, depending primarily on the
time that it takes to saturate the repository, waste form, and
construction of waste containers.

Steady-State Flow Conditions

The quantity of water moving through the repository per unit
time under steady-state conditions will be very small as illus-
trated by the following example. The excavated region in the
repository is assumed to measure 1500 m × 1500 m × 10 m
and has an internal permeability much greater than the sur-
rounding bedrock so that it intercepts a steam of water twice
the width and height of the repository (Figure 5.7). Assuming
a hydraulic conductivity of 10^{-4} m/day (see Figure 5.4—Col-
orado Front Range and Auburn data) and a regional hydraulic
gradient of 10^{-3}, then only 6×10^{-3} m³/day will move through
the repository each day.

If the repository has an overall porosity of 10 percent when
pillars and other nonexcavated portions as well as backfill are
considered, then the total pore volume in the respository is
2.25×10^6 m³. If the flow through the system is 6×10^{-3}/

$K \text{ (bedrock)} = 10^{-4} \text{ m/day}$
$\text{Gradient} (-\frac{\Delta h}{L}) = 10^{-3}$
$A \approx 6 \times 10^4 \text{ m}^2$
$Q \approx 10^{-4} (6 \times 10^4) 10^{-3} \approx 6 \times 10^{-3} \text{ m}^3/\text{day}$
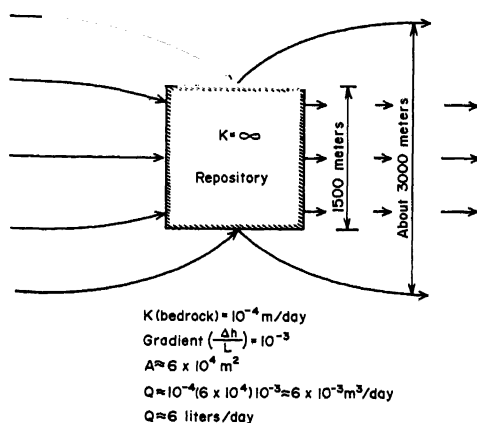$Q \approx 6 \text{ liters/day}$

FIGURE 5.7 Map of a hypothetical repository showing groundwater
flowing through the repository. The width of the zone of groundwater
diversion is only approximate. The height of the repository, measured
perpendicularly to the map, has been assumed to be 10 m.

day, then a once-through, pistonlike displacement of all the
water in the repository would take 3.7×10^8 days or about 10^6
yr. Even if the assumed grouting of larger cracks in the host
rock is not effective and the average permeability is an order
of magnitude larger, the time taken for piston displacement
will still probably be at least 10^4 yr. This is hardly the picture
one obtains when reading the literature where calculations of
the dissolution rates of hazardous materials are based on lab-
oratory batch tests or flow-through tests where simulated waste
is exposed to periodically replaced water or to a constant stream
of water greatly undersaturated with respect to the waste. A
more exact field analogy of these types of laboratory experi-
ments would be the placement of waste canisters directly in
the Mississippi River rather than in a body of groundwater
moving at velocities of much less than a millimeter/day and
water that is already close to chemical equilibrium with respect
to the repository contents. To be sure, a repository will not
have pure piston displacement of water. However, simple cal-
culations such as those given above but taking into account
various degrees of dispersion will all show that the water moves
very slowly in the repository and that thousands, if not hundreds
of thousands, of years will be needed to flush out the water
saturating the repository just once.

Isolated Leaks

The slow drift of small amounts of groundwater through the
entire repository is not expected to present a significant health
problem, at last for periods of many thousands of years. A more
likely problem would be created by an isolated leak that could
develop (1) along a major fracture, (2) through a poorly sealed
shaft, or (3) by a borehole drilled into the repository. Stress
release associated with the construction of the repository could
also open existing small fractures enough to provide significant
leakage. The maximum amount of water coming through an
isolated leak is limited by the low permeability of the rock as
a whole, which would not transmit much water to a permeable
zone. It is further limited by the very low permeability of the
backfill around waste cannisters, which would not allow sig-
nificant water circulation past the cannisters. Under extreme
conditions, a properly constructed repository might be able to
feed a maximum of 1 or 2 L/day to a fracture from a groundwater
system driven by a normal hydraulic gradient. This water could
then contaminate an aquifer, or, if an aquifer does not overlie
the bedrock, the water moving upward could form a small
contaminated spring. The fact that only a small volume of con-
taminated water is involved in these processes is important. A
well penetrating the contaminated aquifer overlying the re-
pository simply would not be developed unless it had a yield
of at least several hundred or, more commonly, several thou-
sand liters per day. Therefore, at least a thousandfold dilution
of the water would be expected before it would be used for
drinking (Figure 5.8).

In addition to the fracture leakage shown in Figure 5.8, a
poorly sealed shaft leading into a repository is also a possible
source of leakage (Figure 5.9). If a natural hydraulic gradient
is assumed to be driving water through the repository and even
if the repository offers no resistance to water movement, it is

Municipal = More than
supply well   200,000 L/day

Domestic well = 2,000 L/day

2 L/day of
contaminated water

Dilution by a factor
of at least 10³.

Waste Repository

$$Q = KA\frac{\Delta h}{L}$$

$$L = (500 + 500)\ m$$

$$A = 10\ m^2$$

$$\frac{\Delta h}{L} = \frac{1}{1000} = 10^{-3}$$

$$K = 10^{-2}\ m/day$$

$$Q = (10^{-2})(10)(10^{-3}) = 10^{-4}\ m^3/day$$
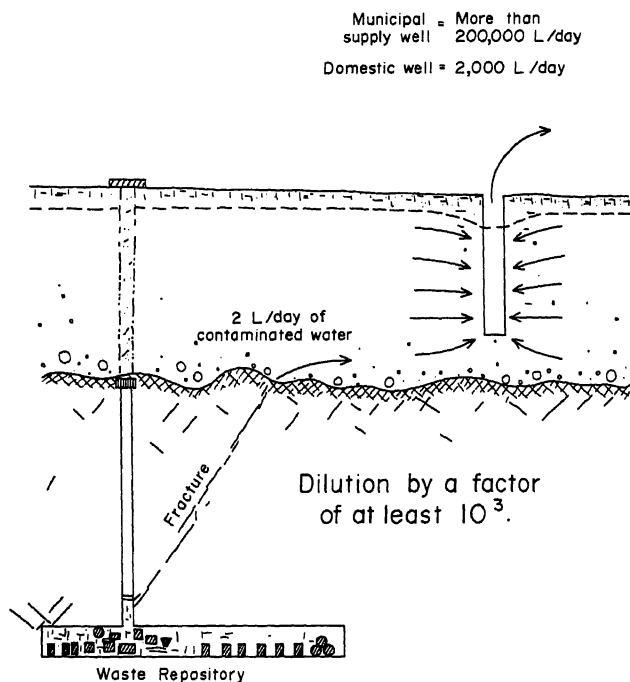
$$Q = 100\ ml/day$$

FIGURE 5.8   Even though small amounts of contaminated water may leave the repository through isolated fractures, this water will most probably be diluted before use, because water wells and springs are rarely developed unless they can yield several hundred to several thousand gallons per day. Although a leak of as much as 2 L/day, as shown in this figure, is considered unlikely, the contaminated water would probably be diluted by a factor of at least 10^3 before use.

FIGURE 5.9   The small potential effect of poor shaft sealing is shown in this hypothetical example of a repository that has an infinite hydraulic conductivity so that the head drop is entirely within the 1000 m of the two filled shafts. Even though the shaft is "sealed" with a semipermeable material, only 100 mL/day of contaminated water flows out of the respository.

difficult to imagine more than a liter per day being circulated through the filled shafts. In fact, if the shafts were sealed by packing them only with silt having a hydraulic conductivity of 10^{-2} m/day (Davis, 1969), the total leakage would be proably much less than 1.0 L/day (Figure 5.9). Shafts will certainly be sealed with material much less permeable than silt, so, in general, shaft sealing is not a major problem unless unusual hydraulic gradients exist between the repository and waters in the more accessible parts of the environment.

DISCUSSION AND CONCLUSIONS

The Federal Nuclear Waste Policy Act of 1982 and subsequent documents such as the U.S. Department of Energy's proposed general guidelines for the location of repositories for high-level radioactive waste (U.S. Department of Energy, 1983) have assumed that the first permanent storage of high-level waste will be in geologic repositories specifically mined for that purpose. If political and social problems can be overcome, there seems to be little doubt that such repositories will be constructed. I have tried to make the case that similar repositories for highly toxic chemical wastes should be considered.

Given identical geologic settings and construction methods, mined repositories for chemical wastes will probably be cheaper per unit volume of waste stored than for high-level radioactive

wastes because most chemical wastes will not generate large amounts of heat after being packaged for the repository. Wastes that might have strong exothermic chemical reactions after closure of the repository are assumed to be excluded from the repository. In contrast, all high-level wastes will generate significant amounts of heat, and close packing of waste in repositories must be avoided in order to prevent very high temperatures from building up in the storage area. In general, however, extraction ratios, mining methods, rock stability, and other factors may be more important than heat dissipation in determining overall construction costs.

Even with the lower costs, however, storage of chemical wastes in large mined repositories will still probably range from a few hundred to a few thousand dollars per cubic meter of waste. Clearly, waste storage in a mined repository will be cost effective only for exceptionally hazardous materials.

As is also true of repositories for high-level radioactive wastes, the long-term confinement of chemical waste in deep repositories will be threatened most by human intrusion and by the transport of chemicals in solution through groundwater migration. Deep burial in metamorphic and plutonic igneous rocks probably will provide the most protection of any geologic materials against human intrusion. The same geologic material will probably also be hydrogeologically satisfactory at depths greater than 300 m, although salt and shale are two geologic materials that may have lower permeabilities (Davis, 1969).

ACKNOWLEDGMENTS

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IV

EXAMPLES

Groundwater Contamination and Aquifer Reclamation at the Rocky Mountain Arsenal, Colorado

6

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ABSTRACT

Groundwater contamination at the Rocky Mountain Arsenal, Colorado, is related to the disposal of liquid industrial wastes and to industrial leaks and spills that have occurred during the 40-yr history of operation of the Arsenal. From 1943 to 1956 the liquid wastes were discharged into unlined ponds, which resulted in contamination of part of the underlying alluvial aquifer. Since 1956, disposal has been accomplished by discharge into an asphalt-lined reservoir, which significantly reduced the volume of contaminants entering the aquifer. In the mid-1970s toxic organic chemicals were detected outside of the Arsenal in the alluvial aquifer. The Colorado Department of Health issued three orders, which called for (1) a halt to unauthorized discharges, (2) cleanup, and (3) groundwater monitoring. Subsequently, a management commitment was made to mitigate the problem. A pilot groundwater containment and treatment system was constructed in 1978; it consists of (1) a bentonite barrier and several withdrawal wells to intercept contaminated groundwater along a 1500-ft length of the northern Arsenal boundary, (2) treating the water with an activated carbon process, and (3) injecting the treated water on the downgradient side of the barrier through several recharge wells. Because of the success of the pilot operation, it is being expanded at present to intercept most of the contaminated underflow crossing the entire north boundary. However, boundary interception alone cannot achieve aquifer restoration at the Arsenal. It is anticipated that the overall final program will also have to include elements of source containment and isolation, source elimination, process modification to reduce the volume of wastes generated, and development of alternative waste-disposal procedures that are nonpolluting. A variety of alternatives have been proposed and are currently being evaluated to determine the most feasible for implementation. The research, planning, and design studies that are necessary to achieve the reclamation goal at the Arsenal illustrate that an effective aquifer restoration program is difficult to design and expensive to implement.

INTRODUCTION

The contamination of a groundwater resource is a serious problem that can have long-term economic and physical consequences because in most cases the problem is neither easily nor quickly remedied. Wood (1972) concluded, "The most satisfactory cure for groundwater pollution is prevention." In many cases where a serious groundwater contamination problem exists, the single most important remedial action that can be taken is to eliminate the source of contamination. But even then, contaminants already in the aquifer will continue to migrate and spread unless some action is taken to immobilize, neutralize, or remove them. Hence, there is often a need to clean up or restore contaminated aquifers.

The "restorability" of a contaminated aquifer is dependent on the hydrogeologic and geochemical properties of the affected aquifer and on the chemical and physical properties of the contaminant. Restoration of a contaminated aquifer is neither technically nor economically feasible in many cases. Factors frequently hindering restoration include (1) the slow diffusive nature of groundwater flow, (2) the difficulty of defining secondary permeability effects, (3) the generally low oxygen content and lack of biologic reactivity in groundwater, (4) the retention of some chemicals in the aquifer because they tend to be sorbed by minerals in the rocks making up the aquifer, (5) the lack of transferability of some restoration techniques from one site to another, and (6) the lack of knowledge about the source of the contamination.

Effective aquifer restoration programs, if technically feasible, are both difficult to design and expensive to implement. Nevertheless, in response to public or governmental demands for positive action in clearly documented cases where groundwater contamination threatens public health, aquifer cleanup programs are being required and instituted more frequently. Some programs are being financed and operated by the federal government. Examples include the Rocky Mountain Arsenal, Colorado, where irrigation and domestic water-supply wells in adjacent areas have been contaminated from industrial wastes stored at the Arsenal, and also Wurtsmith Air Force Base, Michigan, where toxic organic solvents used in aircraft maintenance have entered and spread through the underlying aquifer. Other programs may be implemented because of violations of federal regulations. For example, a recent Justice Department suit was filed in North Carolina under the imminent hazard provision of the Resource Conservation and Recovery Act; the suit asks that the defendants ". . . permanently restore the aquifer to a condition commensurate with safe human use" (*Hazardous Waste News* 2(2), Jan. 21, 1980, p. 12). As an example of an aquifer restoration program being initiated because of state regulations, a chemical company in northern Michigan has come to an agreement with the state of Michigan to remove the contaminants from the soil and groundwater at their former dump site; the projected cost is $12 million to $15 million (*The Wall Street Journal*, Sept. 25, 1981, p. 48).

General management options for restoring water quality in aquifers currently available include the following: (1) eliminate the source of contamination but allow restoration to proceed only through natural flushing, dilution, and geochemical or biological reactions; (2) accelerate removal of contaminants through withdrawal wells, drains, or trenches; (3) accelerate flushing with artificial recharge; (4) install "impermeable" barriers to contain a contaminated area; (5) induce in situ chemical or biologic reactions that would neutralize or immobilize the contaminant; and (6) excavate and remove the contaminated part of the aquifer. The selection of the best approach for a particular situation requires the ability to predict changes in flow and chemical concentration in the aquifer for each possible management alternative. This in turn requires both adequate field data to describe the aquifer systems and the development of accurate simulation models to define the groundwater flow system, pollutant-transport mechanisms, and nature and rate of chemical or biological reactions.
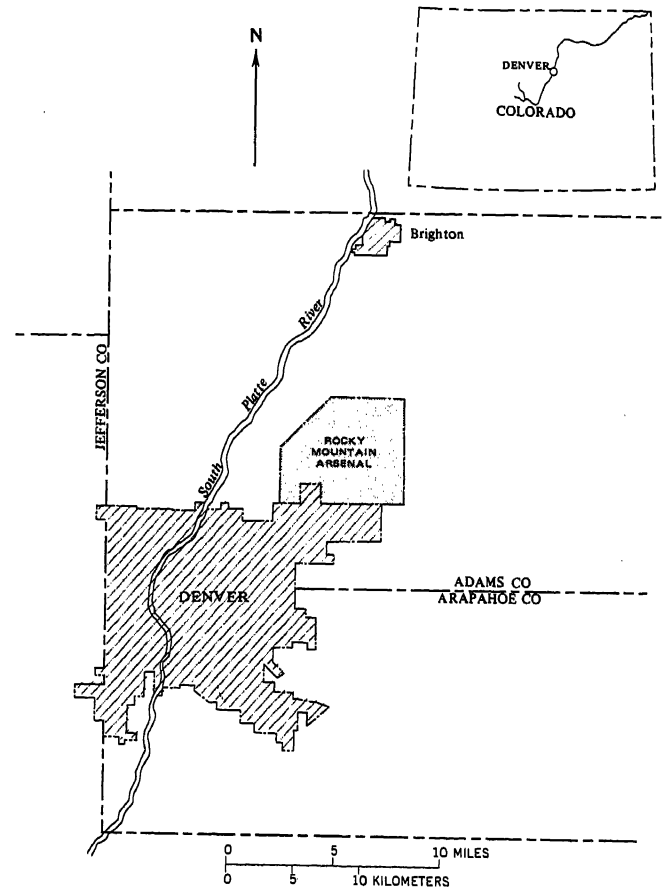
FIGURE 6.1   Location of study area (boundaries are approximate).

This chapter focuses on the groundwater contamination problem at the Rocky Mountain Arsenal, which is located near Denver, Colorado (see Figure 6.1). This area is well suited for serving as a case study to illustrate data requirements, investigative approaches, and management options related to the reclamation of contaminated aquifers because (1) the 40-yr history of groundwater contamination is relatively well documented in the scientific and engineering literature; (2) the geology and hydrology of the area are fairly well known; (3) adequate, though limited, water-quality data are available to calibrate numerical simulation models; (4) the locations and strengths of contaminant sources can be approximately reconstructed; (5) a management commitment has been made to aquifer reclamation; and (6) construction, operation, and evaluation of a pilot reclamation system at the Arsenal have been completed.

DESCRIPTION OF STUDY AREA

History of Contamination

The Rocky Mountain Arsenal has been operating since 1942, primarily manufacturing and processing chemical warfare prod-

ucts and pesticides. These operations have produced liquid wastes that contain complex organic and inorganic chemicals, including a characteristically high chloride concentration that apparently ranged up to about 5000 mg/L.

The liquid wastes were discharged to several unlined ponds (Figure 6.2), resulting in the contamination of the underlying alluvial aquifer. On the basis of available records, it is assumed that contamination first occurred at the beginning of 1943. From 1943 to 1956 the primary disposal was into pond A. Alternate and overflow discharges were collected in ponds B, C, D, and E.

Much of the area north of the Arsenal is irrigated, both with surface water diverted from one of the irrigation canals, which are also unlined, and with groundwater pumped from irrigation wells. Some damage to crops irrigated with shallow ground-water was observed in 1951, 1952, and 1953 (Walton, 1961). Severe crop damage was reported during 1954, a year when the annual precipitation was about one half the normal amount and groundwater use was heavier than normal (Petri, 1961).

Several investigations have been conducted since 1954 to determine both the cause of the problem and how to prevent further damage. Petri and Smith (1956) showed that an area of contaminated groundwater of several square miles existed north and northwest of the disposal ponds. These data clearly indicate

that the liquid wastes seeped out of the unlined disposal ponds, infiltrated the underlying alluvial aquifer, and migrated down-gradient toward the South Platte River. To prevent additional contaminants from entering the aquifer, a 100-acre (0.045-km^2) evaporation pond (reservoir F) was constructed with an asphalt lining in 1956 to hold all subsequent liquid wastes. Although the liner eventually failed, even if the lining were to have remained totally impervious, this new disposal pond in itself would not eliminate the contamination problem because large amounts of contaminants were already present in and slowly migrating through the aquifer.

From about 1968 or 1969 through about 1974, pond C was maintained full most of the time by diverting water from the freshwater reservoirs to the south. This resulted in the infil-tration of about 1 ft^3/sec (0.03 m^3/sec) of freshwater into the alluvial aquifer. This artificial recharge had the effect of diluting and flushing the contaminated groundwater away from pond C faster than would have occurred otherwise. By 1972 the areal extent and magnitude of contamination, as indicated by chlo-ride concentration, had significantly diminished. Chloride con-centrations were then above 1000 mg/L in only two relatively small parts of the contaminated area and were almost at normal background levels in the middle of the affected area (imme-diately downgradient from pond C).

In 1973 and 1974 there were new claims of crop and livestock damages allegedly caused by groundwater that was contami-nated at the Arsenal. Data collected by the Colorado Depart-ment of Health (Shukle, 1975) show that diisopropylmethyl-phosphonate (DIMP), a nerve-gas by-product, has been detected at a concentration of 0.57 part per billion (ppb) in a well located approximately 8 mi (12.9 km) downgradient from the disposal ponds and 1 mi (1.6 km) upgradient from two municipal water-supply wells of the city of Brighton. A DIMP concentration of 48 parts per million (ppm), which is nearly 100,000 times higher, was measured in a groundwater sample collected near the dis-posal ponds. Other contaminants detected in wells or springs in the area include dicyclopentadiene (DCPD), endrin, aldrin, dieldrin, and several organo-sulfur compounds.

The detection of these chemicals, which were manufactured or used at the Arsenal, in areas off the Arsenal property led the Colorado Department of Health to issue cease and desist, cleanup, and monitoring orders in April 1975 to the Rocky Mountain Arsenal and Shell Chemical Company, which was leasing industrial facilities on the site. The Cease and Desist Order called for a halt to unauthorized discharges of contam-inants into surface water and groundwater just north of the Arsenal. The cleanup order applied to all sources of DIMP and DCPD located at the facilities. The third order called for a groundwater monitoring program, the results of which would be reported to the State Health Department on a regular basis. Consequently, a program that included groundwater monitor-ing and studies to determine a means to intercept contaminants flowing across the north boundary of the Arsenal was estab-lished by the U.S. Army.

As a result of continued monitoring, additional contaminants have been identified in the groundwater at the Arsenal. The most widespread of those found are Nemagon (dibromochlo-ropropane) and various industrial solvents. Nemagon contam-
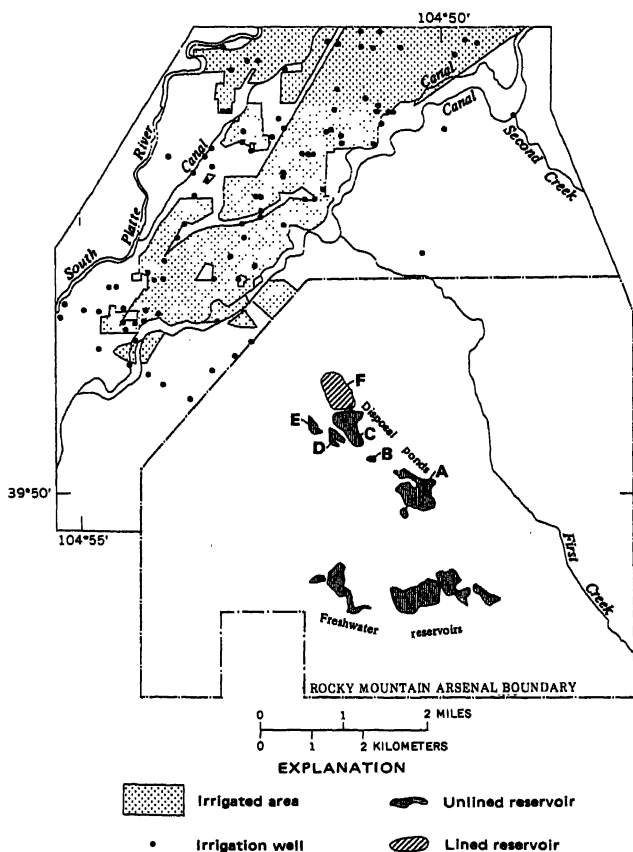

FIGURE 6.2 Major hydrologic features; letters indicate disposal-pond designations assigned by the U.S. Army (Konikow, 1977).

ination has been identified as probably resulting from Arsenal-related activities, whereas the industrial solvents identified are not unique to Arsenal activities. Extremely low concentrations of Nemagon (< 2 ppb) have been found in wells located immediately west of the Arsenal boundary. Other organic contaminants associated with pesticide manufacturing have been found in wells located in a centrally located manufacturing plant area known as the South Plants area. These contaminants probably entered the aquifer from accidental spills and leaks and appear to be migrating from this area very slowly.

Hydrogeology

The records of several hundred observation wells, test holes, irrigation wells, and domestic wells were compiled and analyzed to describe the hydrogeologic characteristics of the alluvial aquifer in and adjacent to the Rocky Mountain Arsenal. Konikow (1975) presented four maps that show the configuration of bedrock surface, generalized water-table configuration, saturated thickness of alluvium, and transmissivity of the aquifer. These maps show that the alluvium forms a complex, sloping, discontinuous, and heterogeneous aquifer system.

A map showing the general water-table configuration for 1955-1971 is presented in Figure 6.3. The assumptions and limitations of Figure 6.3 are discussed in more detail by Konikow (1975). The areas in which the alluvium either is absent or is unsaturated most of the time form internal barriers that significantly affect groundwater flow patterns within the aquifer and, hence, significantly influence solute transport.

The general direction of groundwater movement is from regions of higher water-table altitudes to those of lower water-table altitudes and is approximately perpendicular to the water-table contours. Deviations from the general flow pattern inferred from water-table contours may occur in some areas because of local variations in aquifer properties, recharge, or discharge. The nonorthogonality at places between water-table contours and aquifer boundaries indicates that the approximate limit of the saturated alluvium does not consistently represent a no-flow boundary but that, at some places, there may be significant flow across this line. Such a condition can readily occur in areas where the bedrock possesses significant porosity and hydraulic conductivity or where recharge from irrigation, unlined canals, or other sources is concentrated. Because the hydraulic conductivity of the bedrock underlying the alluvium is generally much lower than that of the alluvium, groundwater flow and contaminant transport through the bedrock are assumed to be secondary considerations compared with flow and transport in the alluvial aquifer. Groundwater withdrawals in the area are predominantly from wells tapping the alluvial aquifer.

Contamination Pattern

Since 1955 several hundred observation wells and test holes have been constructed to monitor changes in water quality and water levels in the alluvial aquifer. The areal extent of contamination has been mapped on the basis of concentration of chloride, DIMP, and other inorganic and organic compounds in

EXPLANATION

—5100— WATER-TABLE CONTOUR — Shows approximate altitude of water table, 1955-71. Contour interval 10 feet (3 meters). Datum is mean sea level

Area in which alluvium is absent or unsaturated
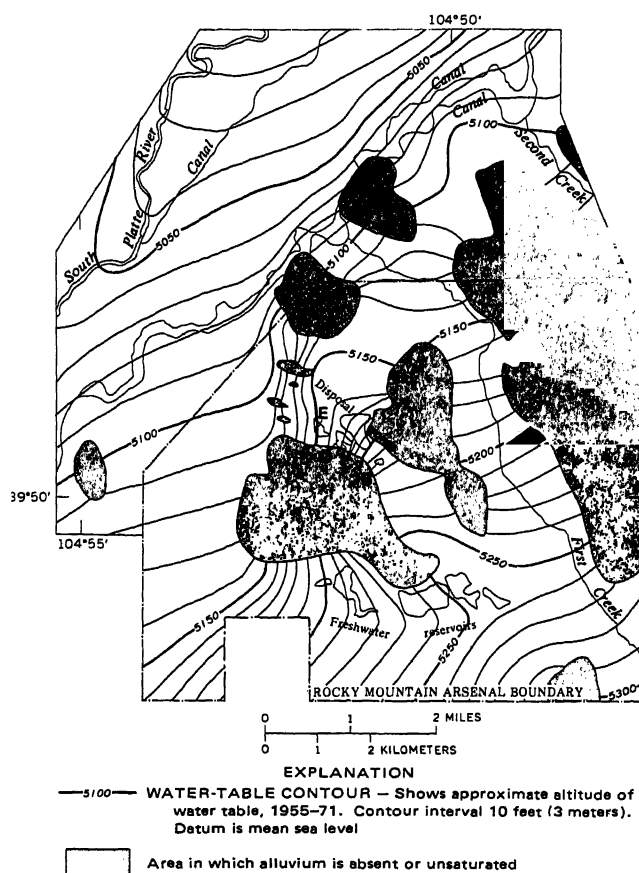
FIGURE 6.3 General water-table configuration in the alluvial aquifer in and adjacent to the Rocky Mountain Arsenal, 1955-1971 (Konikow, 1977).

wells. Chloride concentrations ranged from normal background concentrations of about 40 to 150 mg/L to about 5000 mg/L in contaminated groundwater near pond A. Chloride data collected during 1955-1956 indicate that one main plume of contaminated water extended beyond the northwestern boundary of the Arsenal and that a small secondary plume extended beyond the northern boundary (see Figure 6.4). The contamination pattern shown in Figure 6.4 clearly indicates that the migration of contaminants in this aquifer is also significantly constrained by the aquifer boundaries.

Because chloride generally behaves as a conservative (that is, nonreactive) solute in groundwater, it is often assumed that chlorides can be used to indicate the maximum extent of contamination from a source that contains chloride. But this assumption is not always reasonable because chloride is also a common natural constituent in groundwater. At the Rocky Mountain Arsenal the extent of contamination as indicated by chloride concentration reflects a dilution ratio of about 33:1 from the contaminant source to the definable downgradient limit of contamination. However, the extent of contamination as indicated by some of the organic compounds, such as DIMP (see Robson, 1981), is much greater because they have a zero background concentration and can be detected to trace con-
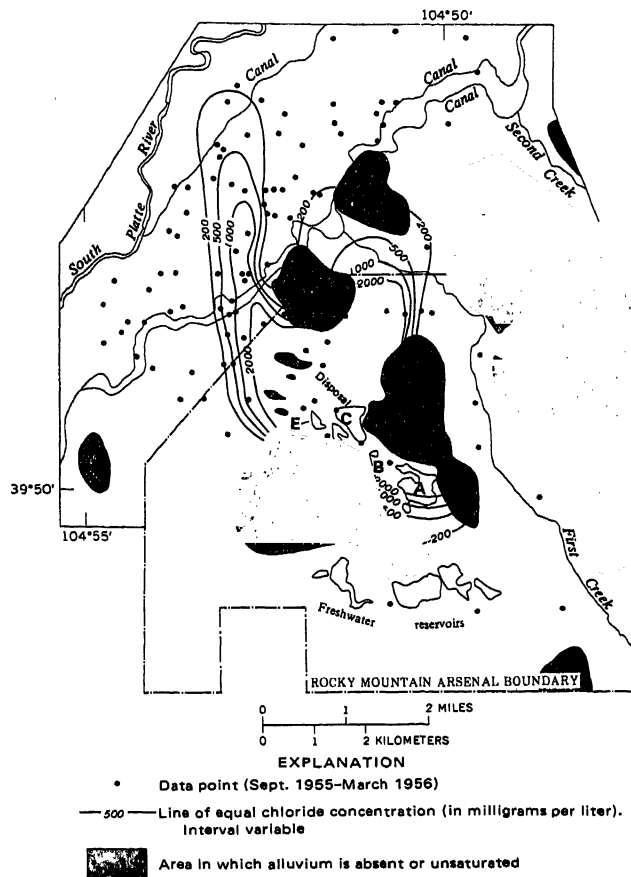
FIGURE 6.4 Observed chloride concentration in 1956 (Konikow, 1977).

centrations that reflect a dilution ratio of about 100,000:1. Other organic contaminants exhibit a much smaller plume, or migration distance, than does the chloride because of reactions that cause them to decay or to be adsorbed. Other differences among shapes and locations of plumes of different contaminants arise because they entered the aquifer at significantly different times and (or) locations within the Arsenal. For example, the Nemagon plume occurs west of the chloride plume because the source of the Nemagon was not from the disposal ponds but apparently from a spill that occurred west of the ponds.

Contaminants have also been detected in several shallow bedrock wells in or near the Arsenal. However, at present there are inadequate data to define the areal extent, depth of penetration, or rate of spreading of contaminants in the bedrock.

APPLICATION OF SIMULATION MODELS

The reliable assessment of hazards or risks arising from groundwater contamination problems and the design of efficient and effective techniques to mitigate them require the capability to predict the behavior of chemical contaminants in flowing groundwater. Reliable and quantitative predictions of contaminant movement can only be made if the processes controlling

convective transport; hydrodynamic dispersion; and chemical, physical, and biological reactions that affect solute concentrations in the ground are understood. These processes, in turn, must be expressed in precise mathematical equations having defined parameters. The theory and development of the equations describing groundwater flow and solute transport have been well documented in the literature. Perhaps the most important technical advancement in the analysis of groundwater contamination problems during the past 10 yr has been the development of deterministic numerical simulation models that efficiently solve the governing flow and transport equations for the properties and boundaries of a specific field situation. Although many of the processes that affect waste movement are individually well understood, their complex interactions in a heterogeneous environment may not be understood well enough for the net outcome to be reliably predicted. Thus, the analysis of groundwater contamination problems can be greatly aided by the application of deterministic numerical simulation models that solve the equations describing groundwater flow and solute transport.

The solute-transport model described by Konikow and Bredehoeft (1978) was used to simulate the movement of chloride through the alluvial aquifer at the Arsenal in an effort to reproduce the 30-yr (1943-1972) history of contamination, to help test hypotheses concerning governing processes and parameters to develop an improved conceptual model of the problem, to aid in setting priorities for the collection of additional data, and to evaluate possible management alternatives (Konikow, 1977). The model included an area of approximately 34 mi^2 (88 km^2). The stringent data requirements for applying the solute-transport model pointed out deficiencies in the data base available at the start of the study. Specifically, it was found that the velocity distribution determined from the water-table configuration mapped in 1956 (see Petri and Smith, 1956) was in part inconsistent with the observed pattern of contaminant spreading. The subsequent quantitative analysis and reinterpretation of available hydrogeologic data, based partly on feedback from the numerical simulation model, led to a revised conceptual model of the aquifer properties and boundaries that incorporated the strong influence of the internal barriers within the alluvial aquifer.

The solute-transport model of Konikow (1977) was calibrated mainly on the basis of the chloride concentration pattern that was observed in 1956 (Figure 6.4). Computed chloride patterns agreed closely with observed patterns, which during the 30-yr history were available only for 1956, 1961, 1969, and 1972. The calibrated model was then used to analyze the effects of future and past changes in stresses and boundary conditions. For example, comparative analyses illustrated that it would probably take at least many decades for this contaminated aquifer to recover naturally its original water-quality characteristics. But it was also inferred that appropriate water-management policies for aquifer reclamation can help to reduce this restoration time to the order of years, rather than decades, for the relatively mobile contaminants. Konikow (1974) also noted that the simulation results showed that a reclamation scheme using a network of interceptor wells would aid in containing and removing the contaminated groundwater.

Robson (1981) developed and calibrated a solute-transport model for DIMP to help evaluate (1) the mechanisms and parameters controlling DIMP migration, (2) future DIMP concentrations in nearby municipal water supply wells, and (3) the effectiveness of various groundwater barrier configurations designed to halt off-Arsenal movement of contaminated groundwater. The model included an area of about 90 mi^2 (230 km^2) and assumed that DIMP is conservative. Using the calibrated model, Robson was able to reconstruct the historical movement of DIMP in the aquifer between 1952 and 1975, to estimate DIMP concentrations in the South Platte River resulting from discharge of contaminated groundwater, and to predict future DIMP concentrations under a variety of assumed management alternatives.

To evaluate more fully the range of engineering approaches or alternatives that would be feasible for construction along the north boundary of the Arsenal, Warner (1979) modeled a smaller part of the aquifer (2.5 mi^2 or 6.4 km^2) in that area in much finer detail. He predicted the impact on DIMP concentration of implementing a variety of interception schemes that incorporated variants of a basic plan that included elements of groundwater withdrawal, a barrier, and reinjection of treated water. Among other findings, Warner (1979) showed that a properly operated hydraulic barrier, consisting of a line of pumping wells, would be just as effective as a bentonite barrier in stopping the movement of DIMP-contaminated groundwater across the northern boundary of the Arsenal.

It is recognized that other organic contaminants of concern may be sorbed or altered by chemical and biological reactions as they move through the aquifer. The movement of a solute that is sorbed will be retarded relative to the movement of a conservative solute. This is beneficial in the sense that in a given time a contaminant that is sorbed will not migrate as far as a conservative contaminant. However, the sorption process could pose a significant obstacle to aquifer reclamation because even after the contaminant source has been eliminated, the sorbed organics could later desorb and continue to migrate through the aquifer, perhaps still posing a hazard after all conservative contaminants have been flushed out of the aquifer. Sorption processes can and have been incorporated into solute-transport models (see Grove, 1976), and this allows a more realistic evaluation to be made of their behavior and response to imposed aquifer reclamation stresses. Although this then presents no great conceptual difficulty, in practice it is quite difficult to determine the coefficients that describe the rates of reactions and exchange capacity of the aquifer material for each individual contaminant.

An overall systems-management model is currently in final development under the sponsorship of the U.S. Army. This computer model is expected to provide a valuable management and decision-making tool to aid in evaluating aquifer reclamation alternatives at the Rocky Mountain Arsenal. The model will be composed of numerous modules, including (1) groundwater flow, (2) solute transport, (3) groundwater interception and control, (4) surface-water control, (5) groundwater and surface-water treatment, (6) cost estimation, and (7) report and graphics output. The model will be evaluated and verified using the Rocky Mountain Arsenal as a test case because of the abun-

dance of historical data there. After verification, selected alternatives for contamination control and elimination at the Arsenal will be modeled with a goal of predicting long-term system responses and costs. If successful, this model will be applied to Installation Restoration programs under way at other locations.

AQUIFER RESTORATION PROGRAM

Response to Cease and Desist Orders

As a result of the Cease and Desist Orders, an Installation Restoration program was established at the Rocky Mountain Arsenal under the direction of the Program Manager for Chemical Demilitarization and Installation Restoration, Aberdeen Proving Ground, Maryland. This office was later reorganized into the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), which currently directs the Installation Restoration program at the Arsenal. The main objective of this program is to limit the migration of contaminants from the Arsenal to the degree required by applicable federal and state regulations. The program is primarily concerned with contamination problems resulting from historical activities on the Arsenal as opposed to ongoing operations.

The Installation Restoration program consists of three major parts or subprograms that include regional groundwater monitoring, contaminant migration control, and elimination of contaminant sources. This program had been organized to allow a phased approach in developing and implementing contaminant control systems, thereby accelerating the reduction of potential environmental hazards. More than $25 million has been expended to date in the Installation Restoration program, excluding the costs associated with construction of the control systems.

A comprehensive groundwater monitoring program was developed based on historical contaminant distribution information and initiated late in 1975. It included sample collection from both on-site and adjacent off-site wells. This monitoring program has been continually updated since that time to include additional wells and analytical parameters as required. Currently, it involves the collection and analysis of samples from 90 to 100 wells on a quarterly basis. The information generated from the monitoring program is used to define the distribution and track the migration of known contaminants, identify new contaminants, develop design criteria for contamination control and treatment systems, and evaluate the operation of existing systems.

The subprogram concerning contaminant migration control at the Arsenal boundaries was initiated in late 1975 with the goal of rapidly eliminating the migration of contaminants off the Arsenal's grounds. Boundary control was the only viable option because of the already wide distribution of contaminants, the long travel times associated with contaminant migration from the sources to the boundaries, and the lack of precise definition of all source areas. Pilot and full-scale boundary control systems have been implemented at the northern Arsenal boundary, and plans have been developed to expand

the treatment system along the northwestern Arsenal boundary. These systems will be discussed in more detail later in this chapter.

Planning for the control and elimination of contaminant sources evolved several years later as additional data became available on specific source areas. The goal is to control or eliminate the contaminant sources on the Arsenal grounds and thereby eliminate the need for boundary control in the future. Studies have been undertaken to aid further identification and definition of contaminant sources, to develop feasible source control and elimination alternatives, and to develop control and treatment systems. A summary of the strategy and progress of this subprogram is given at the end of this chapter.

Contaminant Migration Control at Arsenal Boundaries

Because the contamination that resulted in the issuance of the Cease and Desist Order was detected in surface water and groundwater immediately north of the Arsenal, the primary focus of the Installation Restoration program during 1976 and 1977 was the northern Arsenal boundary. A dike was constructed to stop the migration off the Arsenal of contaminated surface water. Studies were initiated to determine a feasible alternative for stopping the flow of contaminated groundwater off the Arsenal without significantly altering the normal groundwater flow pattern in the area. The concept selected involved interception of the groundwater a short distance south of the northern Arsenal boundary, treatment of the water to remove the contaminants, and reinjection of the treated water at the boundary.

Two methods were proposed for intercepting the flow of groundwater. The first method involved the use of a hydraulic barrier, one or two lines of closely spaced pumping wells that would provide for dewatering of the aquifer along or between the lines. The permeability in the area is sufficiently high for this concept to have worked, but the gradient is shallow and concern was expressed over the potential for excessive recycling of water from the reinjection wells back to the withdrawal wells. As a result of this concern and to provide an additional safety factor, a second method was selected that involved the use of a slurry cutoff wall to form an impermeable barrier between the withdrawal and reinjection wells.

Treatment Process

Late in 1975 a laboratory study was initiated to evaluate various methods for removing organic compounds from representative groundwater samples from the area. Treatment processes investigated include granular activated-carbon adsorption, powdered activated-carbon adsorption, chemical oxidation using ultraviolet (UV) light and ozone, and anionic exchange resins. Key chemical parameters for analysis included DIMP and DCPD. Extensive laboratory studies were conducted using standard isotherm tests for evaluating the carbons and resins and using batch reactor tests for evaluating the UV/ozone process. The anionic exchange resins were dropped from further consideration because of low efficiency and high cost. A series of field studies was initiated on the carbon adsorption and UV/ozone oxidation processes to permit further evaluation.

Powdered activated-carbon adsorption tests incorporating a polymeric coagulant were conducted using a standard Army Erdlator water-treatment unit (chemical addition, mixing, upflow clarification)(Sweder, 1977). Granular activated-carbon adsorption tests were conducted using a dynamic-flow, multicolumn system (Sweder, 1977). UV/ozone oxidation tests were conducted using a continuous-flow, mechanically mixed reactor (Buhts *et al.*, 1978). Granular activated-carbon was found to be more efficient (110 mg of carbon/L of water) in removing the contaminants than was the powdered activated-carbon (200 mg of carbon/L of water). Cost estimates were developed for the carbon adsorption and UV/ozone oxidation processes based on treating 10,000 gallons of water per hour (37,850 L/h). The estimated cost of granular activated-carbon treatment was approximately $2 per 1000 gallons, powdered activated-carbon treatment was approximately $4 per 1000 gallons, and UV/ozone oxidation treatment was approximately $3 per 1000 gallons. As a result of these studies and the immediate availability of proven process equipment, granular activated-carbon was selected for use in the proposed treatment system.

Installation and Operation of Pilot Containment System

Hydrologic and chemical data indicated that the highest concentrations of contaminants were crossing the northern Arsenal boundary in the alluvial aquifer in an area associated with a buried channel in the relatively impermeable bedrock of the Denver Formation. This area is located approximately 1 mile east of the northwest boundary and has a width of approximately 1000 ft (305 m). Because little operational information was available on groundwater contamination control systems similar to the one proposed, the Army decided to install a limited pilot containment system in the area of high-contaminant concentrations and evaluate the possibility of extending the treatment system across the entire affected part of the northern boundary.

The North Boundary Pilot System (NBPS) was constructed and placed in operation in July 1978. It included the following five subsystems: a barrier, dewatering wells, reinjection wells, treatment plant, and monitoring wells. A schematic diagram of the system is provided in Figure 6.5.

The barrier was constructed by filling a 3-ft-wide, 1500-ft-long trench, averaging 25 ft in depth, with a mixture of soil and bentonite clay. The barrier was anchored approximately 2 ft into the bedrock all along the alignment.

The dewatering wells were installed south (upgradient) of the barrier approximately 225 ft apart on a straight line parallel to the barrier. There were six 8-inch-diameter wells placed within 30-inch-diameter gravel-packed holes. Each well was screened throughout the entire saturated portion of the alluvial aquifer. A submersible pump and flow control system were installed at each well site. Water from the wells was pumped through an underground manifold to a single sump at the treatment plant.

The injection wells were installed north (downgradient) of the barrier, approximately 100 ft apart on a straight line between the barrier and the northern Arsenal boundary. There were twelve 18-inch-diameter wells, which were installed in 36-inch-diameter gravel-packed holes. The recharge wells were screened to a point above the water table. Treated water was continuously injected into the recharge wells by gravity flow through an underground manifold system. Sensors and flow control valves were installed in the wells to prevent overflow or surface discharge in the event that a well experienced an excessively high buildup of hydraulic head because of clogging of well screens or other factors.

The treatment plant subsystem was designed to treat 10,000 gallons of water per hour. It consisted of two mixed-media pressure filters, each 4 ft in diameter, and two adsorber vessels (or columns), each 10 ft in diameter and 11 ft high, designed to contain about 20,000 lb (9100 kg) of granular activated carbon. Water from the collection sump was pumped through the filters in parallel to remove suspended material, then through the carbon adsorbers, and finally to the injection wells. Only one carbon adsorber was in operation at any one time. When the DIMP concentration approached 50 ppb, the carbon was replaced. During 1978-1981, replacement was required approximately once every 9 months. The exhausted carbon was transported offsite for regeneration by a commercial vendor. Carbon usage rates ranged from 100 to 150 mg of carbon/L of water. The treatment system was designed to be largely automatic and simple to operate by incorporating automatic backwashing of the filters and sensors for control of pumps and valves.

Ten monitoring wells were installed both upgradient and downgradient of the pilot containment system. They were cased with small-diameter PVC pipe and screened in the alluvial

FIGURE 6.6   Typical gas chromatography/mass spectrometry scan of north boundary pilot treatment system influent.

aquifer. Water levels and chemical quality were monitored periodically to provide information on the effectiveness of the operation of the system.

The cost of the barrier and the wells as constructed in 1978 was $450,000. The facility for housing the treatment system cost approximately $40,000. The treatment equipment was obtained under a lease/service contract agreement with a commercial vendor with an initial cost of approximately $100,000 and a yearly fee ranging from $135,000 to $150,000.

The NBPS operated successfully for a period of approximately 3 yr. For example, during fiscal year 1979, downtime was less than 1 percent of operating time. The granular activated carbon effectively removed the organic contaminants from the groundwater, generally to a level of less than 10 ppb, as illustrated by a comparison of typical gas chromatography/mass spectrometry analyses of the influent (Figure 6.6) and effluent (Figure 6.7) of the treatment system. The flow of groundwater downgradient from the NBPS was essentially unchanged (D'Appolonia Consulting Engineers, Inc., 1979). Preliminary data indicate that the concentration of organics in the groundwater downgradient from the pilot system has diminished significantly.

Expanded Containment System

As a result of the successful operation of the pilot containment system, construction of the expanded containment system was begun in early 1981. The expanded system consists of a 6800-ft barrier ranging from 25 to 50 ft deep, 54 withdrawal wells, and 38 reinjection (or recharge) wells. The expanded barrier effectively intercepts all the contaminated groundwater flowing across the northern Arsenal boundary in the alluvial aquifer. The expanded treatment system is designed to treat 36,000 gallons (136,000 L) of water per hour. The adsorbers used in the pilot operation have been replaced with three pulsed-bed adsorbers designed to contain 30,000 lb (13,600 kg) of carbon
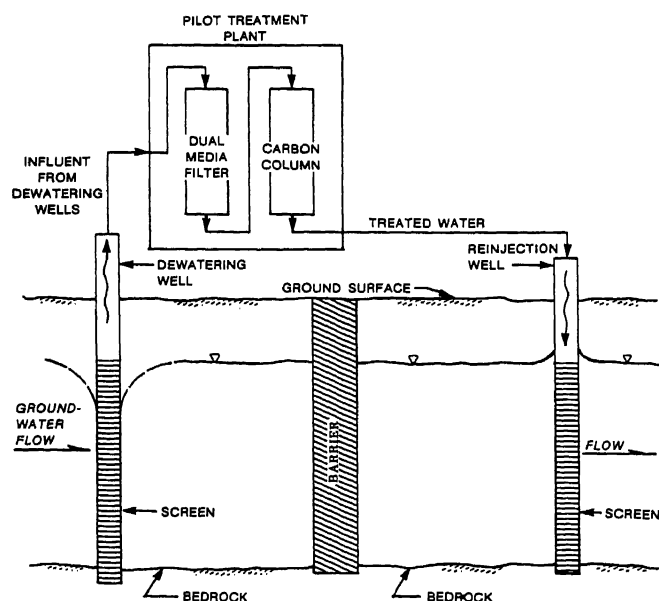

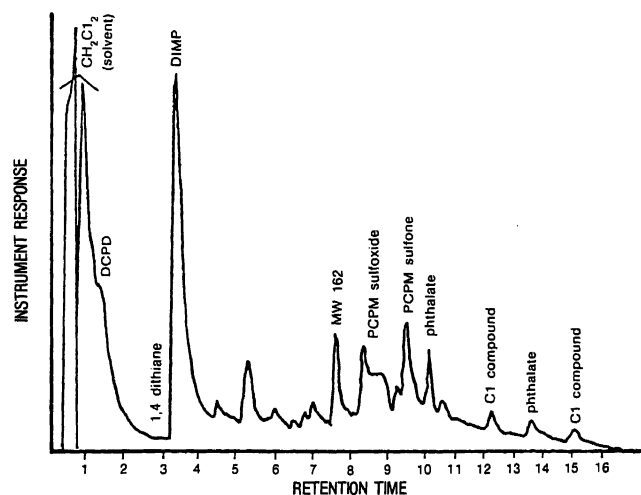FIGURE 6.5   Schematic diagram of north boundary contamination control pilot system.
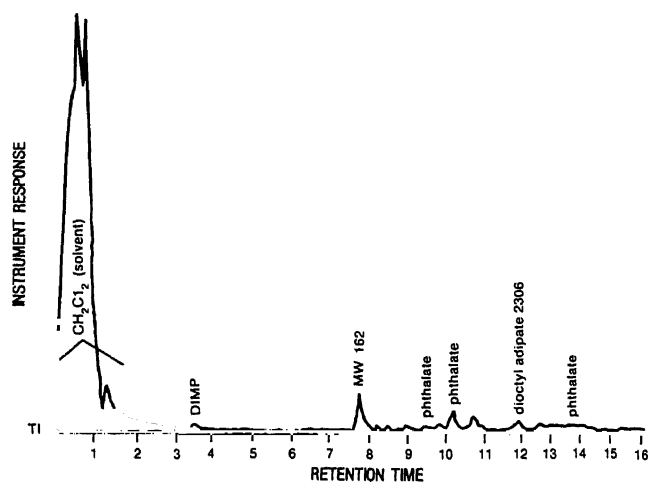
FIGURE 6.7 Typical gas chromatography/mass spectrometry scan of north boundary pilot treatment system effluent.

each. The new adsorbers should be much more efficient than the old ones because the anticipated carbon usage rate is only 25 to 30 mg of carbon/L of water. The mixed-media filters have been replaced with cartridge filters, which are easier to maintain. The whole system is highly automated and will require only intermittent monitoring by a single operator. The estimated cost for the expanded system is approximately $6 million. The expanded system became operational in 1983.

Other Contaminant Migration Control Systems

Concepts have been developed for two additional boundary contaminant migration control systems located along the northwestern Arsenal boundary (Figure 6.8). One system will be located at the southern end of that boundary and the other midway along that boundary. Both systems have been developed primarily to control the migration of low concentrations of Nemagon across the boundary. Both systems will be similar in size to the NBPS and will incorporate granular activated-carbon treatment of the groundwater. The system to be located on the southern end of the boundary (Irondale System) was constructed under the direction of Shell Chemical Company and incorporates a hydraulic barrier for interception of the groundwater, along with the injection wells. It became operational in 1983. The other system, to be constructed by the Army, will incorporate a slurry cutoff wall, withdrawal wells, and reinjection wells, similar to the pilot system. It is scheduled to be operational in 1985.

Planning for Control and Elimination of Contaminant Sources

Contaminant migration control at the boundaries of the Rocky Mountain Arsenal was initiated to stop or severely limit the migration of contaminants off the Arsenal grounds as soon as possible. Owing to the size of the Arsenal and the extent of

the source areas, the boundary control systems could be required to operate for an indefinite period of time. The only way to limit this requirement and the associated cost is to control or eliminate the contaminant sources. Therefore a study was initiated in 1980 to identify and assess existing and innovative control or elimination alternatives that are capable of bringing the Arsenal into compliance with all applicable federal and state environmental laws and regulations. Another study objective was to develop preliminary cost data and technical data for use in a subsequent detailed evaluation and comparison of alternatives. A study team made up of 12 government and independent scientists and engineers was established to conduct and manage the study. A review of historical operations, past study reports, and data from ongoing studies was made to identify, where possible, potential sources of contaminant migration problems.

The next phase of the study involved the development of control strategies. Guidelines and criteria for development of the strategies were required because of the complexity of and relationships between the contaminant sources and migration characteristics. In addition, some degree of commonality of structure or organization among the strategies was needed to enable a comparison and ranking of the alternatives to be developed. As a result, a hierarchical approach and structure for generation and classification of control strategies were developed incorporating five levels of detail ranging from concept to unit operation (Rocky Mountain Arsenal Contamination Control Study Team, unpublished report, August 1981). Each team member individually developed a number of strategies using the hierarchical approach and determined the problem definition and technical data-base deficiencies associated with each scheme. The schemes were then submitted to the group as a whole for integration and evaluation.

Screening criteria were developed to aid in evaluating and comparing the alternative schemes. The goal was to produce
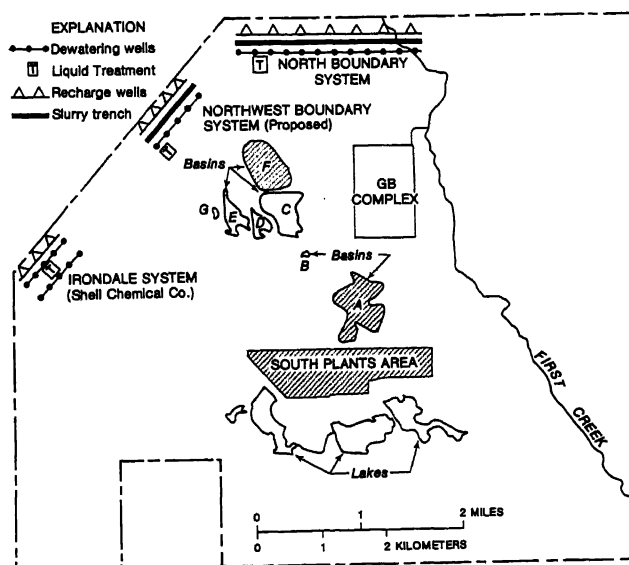

FIGURE 6.8 Location of existing and proposed boundary control systems.

a set of criteria that could be applied at the various hierarchical levels, thereby enabling a general screening of the schemes rather than a detailed evaluation of each one. The major criteria selected for use are as follows:

1. Availability of technology,
2. Amount of additional data required,
3. Cost and time needed to fill data gaps,
4. Life cycle costs—capital and O&M,
5. Compatibility between systems,
6. Degree of risk—environmental and technological,
7. Compliance with regulatory requirements.

The individual schemes developed by the study team members were integrated, evaluated, and screened by the study group as a whole. This work resulted in the presentation of 14 alternative schemes that were recommended for detailed evaluation by the Contamination Control Study Team. The schemes incorporate various aspects of the technologies listed in Table 6.1. The schemes address only the known contaminant sources at the Arsenal and therefore may have to be expanded if additional sources are identified in the future.

In addition to the development of the alternative schemes, the study team identified a number of data gaps concerning both problem definition and technology development that must be filled before final selection of a control or elimination alternative can be made. Studies have been included in the overall Installation Restoration program to fill these data gaps. They include additional hydrogeologic definition of certain areas on the Arsenal, surface-water hydrology definition, technology development for water treatment, and technology development for disposal of contaminated soil and residue. As the data from these additional studies become available, the study team will further evaluate and revise the alternatives as required with the goal of selecting one alternative for implementation.

The implementation of the selected alternative will be conducted using a phased approach. As soon as a particular part

TABLE 6.1   Contaminant Source Control and Elimination Technologies

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Groundwater Interception
   Hydraulic barrier
   Slurry trench
   Dewatering trench (French drain)
Water Treatment
   Adsorption (carbon and resin)
   Chemical addition/coagulation/precipitation
   Filtration
   Membrane separation
   Chemical oxidation
   Activated sludge
   Volatile stripping
   Ion exchange
Contaminated Soil and Residue Treatment
   Incineration
   Fixation/stabilization
   In situ forced leaching
   Excavation and disposal

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of the alternative is defined and design criteria are developed, construction will be initiated. For example, the elimination of Basin F will probably be one of the first major actions initiated because it is known to leak and because the extent and nature of the contamination associated with this area of the Arsenal have been better defined than elsewhere. The control and elimination of known contaminant sources at the Rocky Mountain Arsenal are currently expected to involve a 5-yr construction program that is scheduled to start in 1985. A final cost estimate for the construction program has not been developed, but preliminary estimates range from $50 million to $100 million.

SUMMARY AND CONCLUSIONS

Removing pollutants from a contaminated aquifer may seem to be an almost impossible task. While this may be true for some contaminated aquifers, others may be amenable to one or more plans for artificial reclamation that could significantly accelerate the rate of water-quality improvement in the aquifer. The feasibility of any such reclamation plan would be strongly dependent on the hydraulic and chemical properties of the aquifer, on the type and source of contamination, and on the duration and areal extent of contamination. Because a variety of reclamation plans can be proposed for any one problem, an accurate model of flow and contaminant transport in the aquifer is an invaluable tool for planning an efficient and effective program.

The control and elimination of contaminant migration and contaminant sources at the Rocky Mountain Arsenal represent a large, complex, and costly undertaking (over $25 million has been spent in the Installation Restoration program). An extensive well-monitoring program has been required to define the extent of the contamination and the relationships between the sources and contaminant migration patterns. Control of contaminant migration at the Arsenal boundaries has proved feasible using a system involving groundwater interception, treatment, and reinjection. The system was operated successfully without adversely affecting the flow and distribution of groundwater downgradient from the treatment system, and it has resulted in a significant decrease in the concentration of organic contaminants in groundwater downgradient from the pilot system.

Although boundary-control systems can be used successfully to stop or restrict the migration of contaminants off the Arsenal's grounds, they cannot solve the problem of continued contaminant migration from the source areas to the environment. The overall solution thus involves the control or elimination of the contamination at the sources. A program has been successfully initiated at the Rocky Mountain Arsenal to develop and assess source control and elimination strategies. Through additional data collection and feasibility studies, a single strategy will be selected and implemented using a phased construction approach. The ultimate goal of these activities is to bring the Arsenal into compliance with all applicable federal and state environmental laws and regulations.

The great difficulty and expense involved in mitigating

groundwater contamination problems do not lessen the need to do so; they do illustrate the long-term benefits of planning and designing waste-disposal activities to prevent or minimize future contamination hazards.

ACKNOWLEDGMENTS

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Geologic Problems
at Low-Level Radioactive
Waste-Disposal Sites

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ABSTRACT

Less-than-desirable geohydrologic containment has occurred at three commercially operated and three Department of Energy-operated low-level radioactive waste-disposal sites in the United States. Studies of these sites indicate that the problems fall into eight general categories: "bathtub effect" (water accumulation in filled trenches), trench-cap integrity, erosion, high water table, hydrogeologic complexity, flooding, complex leachate chemistry, and rapid radionuclide migration in groundwater. Problems have been encountered in both high-permeability and low-permeability burial media. All of these problems appear avoidable by applying the following more practical, comprehensive, and commonsense earth-science guidelines for site selection and design:

• A very arid environment eliminates most problems.

• The bathtub effect can be avoided by using physically stable waste forms and by improving the design of the cap.

• Acceptable humid-zone sites can be constructed in permeable media if the water table is sufficiently deep and capillary forces (the "wick effect") are used to divert percolating water from the waste.

• An important factor is to select sites in relatively simple geohydrologic environments to facilitate the prediction of their containment properties.

INTRODUCTION

The United States has been generating low-level radioactive waste since the "atomic age" dawned in the 1940s. Most of this waste has been disposed of by crude, shallow-land-burial techniques, although prior to 1970, significant quantities were also dumped at sea. The term "low-level waste" is a catchall classification lacking specific definition; it includes a variety of radioactive materials that do not fall into one of three other more specifically defined categories of waste: high-level wastes, transuranic wastes, and uranium mill tailings. Some "low-level" wastes are extremely radioactive and may contain relatively large quantities of fission products, with half-lives longer than 25 yr; strontium-90 is an example. Before 1970, low-level wastes were also allowed to contain significant quantities of long-lived

transuranic isotopes such as plutonium-239 (half-life of 24,000 years).

Until 1962, all low-level waste was disposed of by the federal government at federally operated facilities such as Oak Ridge National Laboratory, Tennessee. With the commercialization of nuclear power and expanded use of nuclear medicine and other waste-generation activities, the private sector was given the responsibility for low-level waste disposal, with state and federal regulation.

Between 1962 and 1967, five commercially operated shallow-land-burial sites for low-level waste opened for business at Beatty, Nevada; Maxey Flats, Kentucky; West Valley, New York; Richland, Washington; and Sheffield, Illinois (Figure 7.1). Three of those five sites are now closed because of various technical and legal problems. A sixth commercial site was opened

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A   DOE Storage and Disposal Site
●   Commercial Disposal Site

0   200   400   600   800   1000
|_____|_____|_____|_____|_____|
            Miles
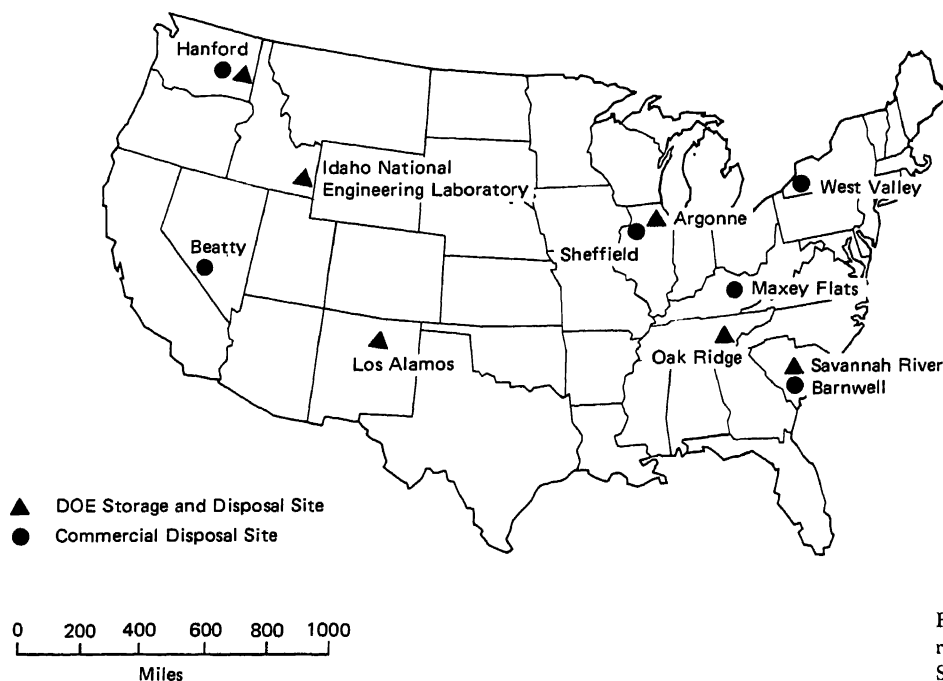
FIGURE 7.1   Location of principal low-level
radioactive-waste-disposal sites in the United
States.

in 1971 at Barnwell, South Carolina, and currently remains open. That site plus the Beatty and Richland sites now handle all of the nation's commercially generated low-level wastes, which amount to some 75,000 m³/yr.

In addition, federal government nuclear research and defense activities generate approximately an equal volume of low-level wastes per year, which is buried at five major U.S. Department of Energy (DOE) facilities and several minor sites (Figure 7.1).

Because the locations of the three currently operating commercial sites do not represent a politically acceptable or geographically equitable distribution of the wastes, and because their limited capacity is not adequate for anticipated waste-generation rates, the need for additional sites has been recognized over the past few years. Congress passed the Low-Level Waste Policy Act in 1980, which mandates that states establish additional sites on a regional basis before 1986. DOE will also require additional burial sites within the next several years. It would seem prudent, therefore, to apply the best earth-science criteria to the screening, selection, and design of new sites. The source of some of our best geohydrologic information for that purpose is the performance record of the older sites. The principal concern, of course, is to protect groundwater and surface-water supplies from contamination.

SITE-SELECTION CRITERIA FOR EXISTING SITES

During the period when the six commercial disposal sites were chosen, there were no uniform regulations providing comprehensive site-specific geohydrologic criteria to be applied to the selection and operation of disposal sites. The Atomic Energy

Commission had some general guidelines and performance standards for low-level sites but allowed states to set their own standards if they assumed responsibility for regulation sites.

It is not clear what specific geohydrologic criteria (if any) were applied to each of the six sites. It is apparent that the criteria were simplistic and that the dominant criterion for the humid zone sites was that they be placed in low-permeability, clay-rich sediments or in shale. Another important criterion was that the site be underlain by easily excavatable material. The West Valley, New York, site is in fairly uniform, clay-rich glacial till; the Maxey Flats, Kentucky, site is in a low-permeability (but fractured) shale. The Sheffield, Illinois, site was apparently intended to be in clay-rich glacial till, but it was discovered later that the till contained some permeable, gravelly sand lenses. The Barnwell, South Carolina, site was placed in sandy, clayey coastal plain sediments, which are somewhat more permeable than the tills and shales of the other eastern sites.

For the two arid western sites (Richland, Washington, and Beatty, Nevada) the low rainfall rate appears to have been the dominant geohydrologic criterion applied. Those sites have an average annual rainfall of 165 and 101 mm (6.5 and 4 inches), respectively, and are both situated in mixed coarse-grained unconsolidated sediments (Robertson, 1980).

The DOE sites were apparently selected with even less definitive and documented earth-science criteria. The dominant approach appears to have been to locate the sites within the bounds of the facility reservation. Geohydrologic factors appear to have been a secondary consideration.

Among the geologic media and hydrologic settings selected for the DOE sites are the following: mixed glacial tills, coastal plain sediments, thin floodplain sediments on permeable basalt, coarse-grained glacio-fluvial sediments, fractured perme-

able shales, and fractured tuff. Permeability of these materials ranges from about 10^{-9} to 10 cm/sec. Annual precipitation rates range from about 101 to 1370 mm (4 to 54 inches). Water-table depths range from less than 2 m to a few hundred meters (Robertson, 1980).

PROBLEMS ENCOUNTERED AT EXISTING SITES

Several geohydrologic problems have been encountered at existing sites, which can be partially attributed, in retrospect, to inadequate attention to earth-science criteria in site selection and to inadequate site characterization and design. Nearly all of these problems or shortcomings are related to eight factors: "bathtub effect," trench-cap integrity, erosion, high water table, hydrogeologic complexity, flooding, complex leachate chemistry, and rapid radionuclide migration. Nearly all of these factors are interrelated and interdependent.

Bathtub Effect

This effect occurs in wet-climate, low-permeability sites such as West Valley, New York, and Maxey Flats, Kentucky. (Although the principal medium at Maxey Flats is low-permeability shale, the shale contains a few thin beds of fractured sandstone with higher permeability.) Because of differential subsidence, desiccation cracks, and other reasons, the trench-capping material on waste-filled trenches becomes increasingly permeable, thus enhancing the infiltration of precipitation. Water then accumulates in the trenches, sometimes seeping out on the ground surface, carrying leached radionuclides. This problem has often been blamed more on the low permeability of the natural media than on the high permeability of trench caps and backfill material.

Trench-Cap Integrity

This problem is closely related to the bathtub effect. As wastes and backfill material decompose and compact, settlement cracks, depressions, and holes develop in the capping material, providing ready avenues of water infiltration. Desiccation cracks can also develop in clay-rich caps during extended dry periods, with the same hydrologic effect.

Erosion

Erosion has been a problem or is considered to be a potential problem at some sites. At the Sheffield, Illinois, site, for instance, unanticipated rapid runoff from large snow accumulation caused undesirable erosion and piping problems in 1979 (James B. Foster, U.S. Geological Survey, personal communication, 1979). Questions on potential long-term erosion prob-

lems have been raised at sites such as West Valley, Beatty, and DOE's Idaho National Engineering Laboratory (INEL).

High Water Table

In a few cases (Oak Ridge National Laboratory and West Valley, for instance), burial trenches were excavated below the water table, thus providing constant submergence and leaching of some wastes. Although that condition might be undesirable, it is not necessarily detrimental if groundwater flow rates are sufficiently slow. In some places at the Oak Ridge site, raising the ground surface by fill material actually induced the upward movement of the water table into the waste (Webster, 1979).

Hydrologic Complexity

Hydrologic complexity has been a problem of varying magnitude at many sites. It simply means the sites proved to be physically more complex than originally anticipated, so that long-term (or even short-term) performance predictions were found to be in error. An example is the complex of glacial-fluvial stratigraphy of the Sheffield, Illinois, site (Foster and Erickson, 1979). The original array of test wells used to characterize the stratigraphy was not adequate to define the distribution of permeable sand units. In another example at the Maxey Flats, Kentucky, site, groundwater flow is controlled by fractures (Zehner, 1979); although the average flow rate may be very low, it cannot easily be characterized quantitatively.

Flooding

Flooding has been a problem on the INEL disposal site. On two occasions, in 1962 and 1969, the site has been inundated by local runoff (Barraclough et al., 1976). Remedial engineering measures have since been taken to reduce the likelihood and magnitude of further flooding. Although INEL is an arid site with 203 mm (8 inches) of annual rainfall, the problem resulted in open burial trenches' being filled with water and considerable infiltration of water over the entire site. Flooding was caused by a combination of unusual meteorologic conditions and the location of the site within a topographic basin.

Complex Leachate Chemistry

Because of the variety and complexity of low-level waste, the chemical characteristics of leachates from buried wastes are comparably variable and complex. Many nonradioactive organic and inorganic compounds are buried with the waste or result from the biological and chemical decomposition of trash materials. This results in unpredictable oxidation states of some nuclides and chemical complexation with chelating agents and other ligands. Such complexes can be more mobile in groundwater than can uncomplexed cations. At the Maxey Flats site,

for example, plutonium has been observed in trench leachates and in groundwater in chemically complexed forms (Cleveland and Rees, 1981).

Rapid Radionuclide Migration

All the above-mentioned problems can contribute and have contributed to the migration of waste radionuclides away from burial sites at faster rates or in different directions than expected. Contributing to this problem at some sites is the relatively high permeability of the media in which the wastes are buried. This has been a concern at Oak Ridge, Maxey Flats, Sheffield, Barnwell, and INEL, among others. Plutonium and other isotopes have migrated laterally through a thin permeable fractured sandstone bed at Maxey Flats. Tritium has migrated vertically and laterally through permeable sand layers at Sheffield and Barnwell, and several isotopes have migrated vertically through permeable basalt at INEL.

Thus, an apparent dilemma arises: if both low-permeability and high-permeability sites can have problems, are both conditions unacceptable or is one preferable to another?

POSSIBLE ANSWERS TO THE QUESTIONS

None of the problems observed at existing sites has been disastrous in terms of harm to human life—there is no evidence of public drinking-water contamination nor harmful radiation exposure to humans due to groundwater contamination from these sites. However, the problems are nonetheless undesirable. Essentially, all of these potential problems at future sites appear amenable to practical solutions by applying more sensible and appropriate earth-science criteria to site selection, characterization, design, and operation.

Bathtub Effect and Trench-Cap Integrity

There are at least three potential solutions to the bathtub effect:

1. Require stable noncompactable waste forms and backfill, combined with more stable, low-permeability trench capping.
2. Place trenches in permeable media above the water table with low-permeability trench cap.
3. Locate the site in a very arid environment.

These options are all specified in the proposed Nuclear Regulatory Commission's low-level waste management regulations, 10 CFR Part 61 [*Federal Register 46*(142), July 24, 1981]. It is generally agreed that low-permeability clay-rich sediments can be good burial media when used conjunctively with improvements in waste form and capping technology.

Geohydrologic Complexity

Problems related to conditions of geohydrologic complexity can, of course, be reduced by avoiding media dominated by secondary permeability features or complex stratigraphy. Complexity is relative; consequently, this is a subjective criterion, requiring judgment.

High Water Table

In addition to specifying minimum depth to the saturated zone, the potential occurrence of a high water table can be avoided by reducing the permeability of trench caps, providing good land-surface drainage, and avoiding large increases in land-surface elevation from backfilling. If the hydraulic conductivity of the burial medium is below 10^{-6} or 10^{-7} cm/sec, groundwater flow rates will be slow enough that radionuclide migration is dominated by molecular diffusion. In such circumstances, it is not really important to exclude groundwater from the waste. In Canada, for instance, burial below the water table is permitted in glacial clays with low hydraulic conductivity.

Complex Leachate Chemistry

The problems resulting from complex leachate chemistry can also be reduced by simplifying waste forms; requiring more stable, less leachable wastes; and excluding potential complexing agents from the waste.

Rapid Radionuclide Migration in High-Permeability Media

This problem can be avoided by applying the following guidelines to sites in high-permeability materials:

1. Waste must be placed well above the water table.
2. Contact of waste with infiltrating water must be minimized by stable, low-permeability trench covers or by effective use of the "wick effect." The wick effect results from natural capillary suction of certain types of unsaturated sediments, which draws water away from wastes. This principle has been effectively demonstrated in the field by French researchers (Rancon, 1980). The Barnwell, South Carolina, site appears to have benefited by this effect, but conclusive evidence is not yet available.

CONCLUSIONS

The key to effective isolation of low-level radioactive waste (or any hazardous waste) is minimizing contact of water with the waste and minimizing migration rates in groundwater. Perhaps the most fundamental lesson learned from examining the history of earth-science aspects of existing sites is that no single dominant geohydrologic criterion is more critical than others for every site. Criteria for all facets of the disposal system must be considered together to obtain good performance. Reliance on a single criterion, such as burial in low-permeability clay, while ignoring other criteria such as waste form and trench caps, can lead to failure. It is apparent that both the Nuclear Regulatory Commission and the Department of Energy have recognized these problems and the potential solutions. Consequently, both organizations are incorporating, in one form

or another, the solutions recommended here into their re-
spective regulatory criteria and technical guidelines. Because
of lessons learned from earlier and current disposal practices,
the next generation of low-level radioactive-waste-disposal sites
promises to be much more reliable from an earth-science point
of view.

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Groundwater Flow Modeling Study of the Love Canal Area, New York

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ABSTRACT

Increasing awareness of the problems presented by hazardous waste sites is leading toward an increased interest in, and application of, groundwater models. During the fall of 1980, a groundwater modeling study was conducted at the Love Canal area, Niagara Falls, New York. Flow models were used to aid in data reduction and analysis and to attempt prediction of groundwater movement. Both slug tests and aquifer tests were analyzed. The conceptual framework for the hydrogeologic units underlying Love Canal consists of a shallow water-table system of silts and fine sands and a deeper confined system in the Lockport Dolomite. The intervening confining layers consist of lacustrine and glacial clays. Modeling in the dolomite focused on characterizing the aquifer and assessing the potential for its contamination. Best judgment indicates that for the Lockport to be contaminated, the confining bed would have to be breached. Analysis of remedial action for the Lockport Dolomite indicates that three interceptor wells at the south end of the canal, pumped at only 32.3 m^3/day, would reverse the flow of groundwater to the river and provide an adequate halt to migration of potential contaminants to the river.

INTRODUCTION

The U.S. Environmental Protection Agency identified a need to assess the groundwater hydrology of the Love Canal area, Niagara Falls, New York. As part of this assessment, groundwater flow models were used to aid in data reduction and analysis and to attempt prediction of groundwater movement and contaminant migration. The modeling effort was started on August 20, 1980, and completed December 1, 1980.

The objectives were to (1) devise a conceptual framework, (2) assist in data collection, (3) design and analyze aquifer tests, (4) predict system behavior, and (5) assess uncertainty. The technical approach involved the use of groundwater flow models, which were used to help interpret and predict the behavior of groundwater flow and convective transport at Love Canal. Since hydrodynamic dispersion is neglected, arrival times may be slightly underestimated.

This chapter summarizes some of the work performed during this study. Results are presented for the aquifer test analysis and for modeling the Lockport Dolomite aquifer. The shallow system and remedial action modeling and analysis are presented elsewhere (Mercer *et al.*, 1981; Silka and Mercer, 1982).

BACKGROUND

The Love Canal site is located on the east side of Niagara Falls, New York. The landfill at Love Canal was operated for nearly 30 yr and occupied a surface area of approximately 16 acres with the south end 400 m from the upper Niagara River near Cayuga Island. The canal varies from about 3 to 11 m in depth with the original soil cover varying from 0 to 1.8 m in thickness (Leonard *et al.*, 1977).

Figure 8.1 shows the typical strata at the Love Canal site. The soil layers are underlain by glacial till, which in turn is underlain by bedrock consisting of the Lockport Dolomite. In general terms, the groundwater hydrology includes (1) a shal-

DEPTH   DESCRIPTION

1.8-2.5' (0.6-0.8 m)	Land Surface Clayey Silt Fill
4.0-5.5' (1.2-1.7 m)	Silty Sand
7.5-8.5' (2.3-2.6 m)	Very Firm - Extremely Firm Silty Clay
10.5-11.5' (3.2-3.5 m)	Transition Zone
19.0-27.0' (5.8-8.2 m)	Soft Silty Clay
34.0-42.0' (10.4-12.8 m)	Glacial Till
	Lockport Dolomite (Ranges in thickness from approximately 100 to 150 feet/ 30 to 46 meters)
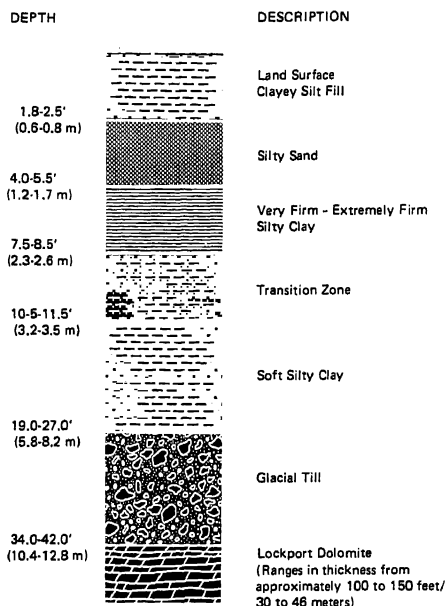
FIGURE 8.1   Typical strata in Love Canal landfill area (modified from Conestoga-Rovers & Associates, 1978).

low system that is seasonally saturated and consists of the silt fill and silty sand and is underlain by (2) beds of confining material composed of clay and till that overlies (3) the Lockport Dolomite, which is underlain by the relatively impermeable (4) Rochester Shale.

Lockport Dolomite

The Lockport Dolomite is overlain by leaky confining beds and underlain by the relatively impermeable Rochester Shale (Johnston, 1964) and is fairly continuous in the Niagara Falls area. Both artesian and water-table conditions occur in this fractured system, with the upper 3 to 4.6 m being the most permeable. Hydrogeologically, the dolomite in the Niagara Falls area probably is bounded on the south by the upper Niagara River (see Figure 8.2). It is bounded toward the west by the lower Niagara River gorge. The dolomite thins northward, where it is bounded by its outcrops in the Niagara escarpment.

Under natural conditions, recharge occurs at the contact with the upper Niagara River near the falls and at an elevation high that is just south of the Niagara escarpment. Discharge occurs as seepage faces and springs at the lower Niagara River, along the Niagara escarpment, and along parts of the upper Niagara River away from the falls.

A generalized potentiometric map developed from historic records for the Lockport Dolomite (Johnston, 1964) is shown in Figure 8.2. The contours are highly idealized because the data were either (1) absent, (2) representative of several layers within the dolomite, or (3) collected over a two-year span during 1961-1962.

A well hydrograph in the area indicates that flow is quasi-steady state. "Quasi" is used because seasonal variations of about ±0.6 m are believed to be imposed on the steady-state condition in the upper part of the dolomite. Furthermore, since this study occurred in the fall, it is expected that the water levels represent seasonal lows.

FIGURE 8.2   Generalized potentiometric surfaces for the Lockport Dolomite.
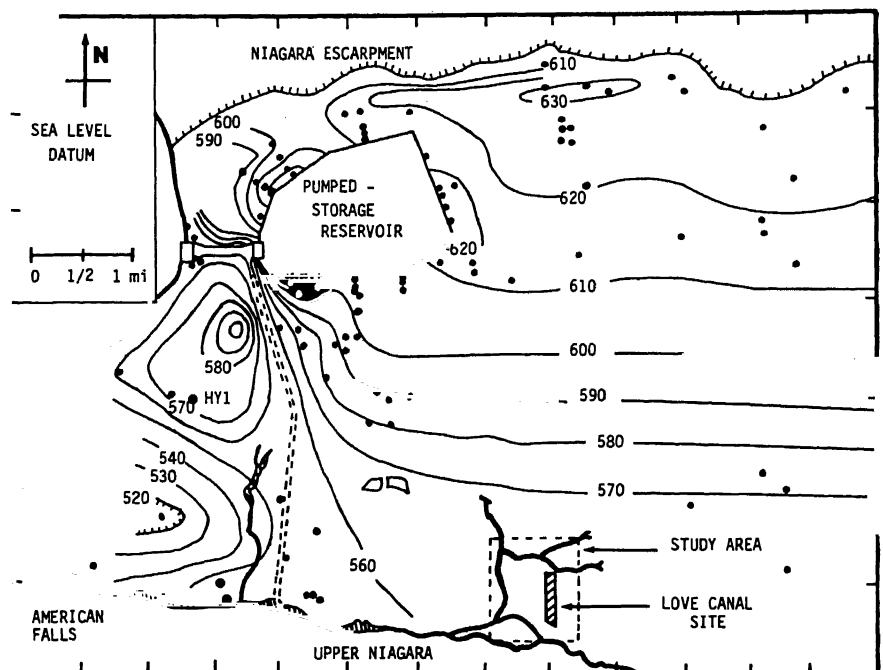
Shallow System

The shallow system at Love Canal is located in the upper units of silty sand and silt fill. It is probably bounded toward the north and west by creeks and toward the south by the Little Niagara River. Before remedial actions were taken, groundwater flow was probably toward the surface drainage, with the overall flow toward the south and the upper Niagara River.

The soils in this area consist of the Canadaigua-Raynham-Rhinebeck association characterized by somewhat poorly drained to very poorly drained soils having a dominantly medium- to fine-texture subsoil (U.S. Department of Agriculture, 1972). These soils are silty loam to silty clay loam (ML to CL in the Unified Soil Classification). Previous work in the area has typified the soils as shown in Figure 8.1 (Conestoga-Rovers & Associates, 1978). Underlying the lacustrine sediments are glacial tills.

The shallow system can be summarized as follows:

1. Silty sand and silt fill; approximately 3.7 m thick; hydraulic conductivity is greater than or equal to 10^{-7} m/sec (Hart, 1978).

2. Hard clay, transition clay, soft clay; 3.4 m thick; hydraulic conductivity is 10^{-10} to 10^{-11} m/sec (Leonard *et al.*, 1977).

3. Glacial till; 4.6 m thick; hydraulic conductivity is probably similar to that of clays (Glaubinger *et al.*, 1979).

In addition to these units, storm-sewer and sanitary-sewer excavations as well as swales may act as conduits. Ebert (1979) describes the swales as old drainage ways up to 3 m deep and 12 m wide in their original state. Many of these old drainage ways have been filled with miscellaneous material.

AQUIFER TESTING ANALYSIS

Aquifer testing was designed, and subsequently modified, to characterize certain aspects of the groundwater system at the Love Canal site. These included the following:

1. Determination of the horizontal hydraulic conductivity and storage coefficient of unconsolidated glacial units and the Lockport Dolomite;

2. Determination of the variation of hydraulic conductivity with depth in the dolomite;

3. Determination of the hydraulic connection between the more permeable upper zones of the shallow system and the dolomite, that is, the vertical component of hydraulic conductivity in the till and tight lacustrine sediments; and

4. Determination of the interconnection (vertical hydraulic conductivity) of permeable layers in the Lockport Dolomite.

The tests used at the site included constant-pressure tests and constant-discharge tests in the Lockport Dolomite and a falling-head test in the overburden and till units. Except for the constant-discharge test, the results of the testing are difficult to quantify. Therefore, only the constant-discharge test in the dolomite is described here and is presented for illustrative purposes.

The basic solution used for the constant-discharge pumping test is the Theis (1935) solution

$$s = \frac{Q}{4\pi T} \int_{\frac{r^2 S}{4Tt}}^{\infty} \frac{e^{-u}}{u} \, du, \qquad (8.1)$$

where s is the drawdown (L); r is the distance from pumped well to observation well (L); Q is the discharge rate (L^3/t); t is the time after start of pumping; T is the transmissivity (L^2/t); and S is the storage coefficient (dimensionless).

Although the long-term pumping test in the dolomite at the site was designed to run at a constant-discharge rate, the actual pumping rate declined during the test. An approximate solution for these conditions can be obtained by using the principle of superposition in conjunction with the basic solution. The procedure involves representing the variable pumping rate by a series of pumping periods having constant rates. The approximate solution is then given by

$$s = \frac{1}{4\pi T} \sum_{j=1}^{m} (Q_j - Q_{j-1}) \, W(u_j), \qquad (8.2)$$

where j is the particular pumping period, m is the total number of pumping periods, $W(u)$ is the exponential integral in Eq. cedure involves representing the variable pumping rate by a cedure is further detailed by Earlougher (1977).

Eqs. (8.1) and (8.2) provide forward solutions to the groundwater response. In this field test the inverse solution is required; that is, from observed water-level changes, the hydrologic parameters T and S need to be determined. In order to solve Eq. (8.2), a least-squares minimization technique is used. That is, to find T and S,

$$\sum_{i=1}^{n} [s_0(r_i, t_i) - s_c(r_i, t_i)]^2 \qquad (8.3)$$

is minimized, where s_0 is the observed drawdown, s_c is the calculated drawdown, i refers to a particular observation, and n is the total number of observations.

Data were used from 12 observation wells and the pumping well. Measurements were continued at three observation wells for 2 h after the pump was shut down. With all of these data, there are several alternative ways to partition them for analysis. Two obvious ways are (1) match all the observations using one transmissivity value and one storage coefficient value (Case A), and (2) match the data for each well independently, calculating a separate T and S for each well (Case B). Both methods were used in this analysis. Comparing the results of both cases provides a measure of validity in the analysis.

The results of matching the data are presented in Table 8.1. Using all available data and matching all the wells with one T and S led to values of 0.0014 m²/sec and 1.49 × 10^{-4}, respectively. The mean deviation between observed values and calculated values using the above T and S was 0.12 m. Fitting the individual well data led to better matches of the data. For this case the transmissivity values were between 0.001 and 0.0035 m²/sec and the storage coefficient values were between 0.343 × 10^{-4} and 3.12 × 10^{-4}. As noted, the matches on individual wells were better—mean deviations for each well were between 0.010 and 0.064 m.

Other results from aquifer testing are not presented but may be found in Mercer *et al.* (1981). The results of the aquifer

TABLE 8.1 Summary of Results of Pumping and Recovery Test Analysis

Matching Group	Well	T (m²/sec)	$S \times 10^{-4}$	Mean Deviation, m
Case A (all wells together)	—	0.0014	1.490	0.119
Case B (individual wells)	38	0.0035	2.370	0.010
	44	0.0031	1.650	0.014
	48	0.0025	0.343	0.019
	50	0.0018	0.483	0.032
	56	0.0019	0.825	0.016
	67	0.0017	1.750	0.025
	68	0.0010	1.330	0.019
	71	0.0019	1.500	0.020
	79	0.0016	0.428	0.033
	80	0.0014	1.290	0.025
	86	0.0017	3.120	0.049
	89	0.0010	2.000	0.064
	Average	0.0020	1.420	—

testing partially fulfilled the original test objectives. The following conclusions were drawn from the above analysis:

1. The 22-h discharge test in the Lockport Dolomite provided an average field transmissivity of 0.0014 m²/sec and storage coefficient of 1.5×10^{-4}. These values are consistent with other values determined for the Lockport Dolomite in the Niagara vicinity.

2. Because many of the observation wells were completed only about 1 m into the dolomite, and because they responded quickly to the pumping from a well screened at a deeper level, the upper permeable zones of the dolomite appear to have significant vertical permeability.

3. The Lockport Dolomite is heterogeneous but less so than would normally be anticipated for carbonate aquifers.

4. The packer test results for the dolomite were inconclusive. Consequently, the regional observations of Johnston (1964) regarding the variation of hydraulic conductivity with depth are still assumed applicable to the site. Examination of the core description also supports Johnston's contention that the primary water-bearing zones are located in the upper zones of the Lockport Dolomite.

5. The slug tests in the overburden wells provided an estimate of the hydraulic conductivity of the lacustrine sediments and till. Both values are on the order of 3.04×10^{-10} m/sec and indicate relatively impermeable material.

6. The shallow material tested at the slug test site was also relatively impermeable (on the order of 3×10^{-10} m/sec). However, this unit was quite clayey. Because the shallow silty-sandy units are highly variable, this one estimate is probably not representative of the shallow system at the site.

7. No estimates of storage properties for the overburden wells could be determined from the slug tests.

LOCKPORT DOLOMITE MODEL

There are several numerical models that are appropriate for simulating flow in the Lockport Dolomite. The approach taken was to vertically average the flow and aquifer parameters through

the aquifer thickness. The boundary condition at the bottom is probably no-flow, since below the first 4.6 m parts of the Lockport Dolomite are relatively impermeable. At the top, the boundary condition is probably head-controlled flux representing leakage through the confining beds. A groundwater flow model that handles these areal flow conditions is that presented by Trescott et al. (1976). Important assumptions include the following:

1. Groundwater flow and aquifer parameters in the Lockport Dolomite are vertically averaged.

2. Quasi-steady-state flow is assumed; that is, although there are seasonal variations, the system over an extended period of time does not change hydrologically from the seasonally averaged surface. This assumption is based on the few well hydrographs available in the Niagara Falls area.

3. The aquifer in the Lockport Dolomite is assumed to be under leaky artesian conditions everywhere.

4. The aquifer transmissivity near the escarpment is assumed equal to 4.58×10^{-5} m²/sec. Because of the analysis of tests at the Love Canal site, and because of the higher aquifer transmissivity near the river (Johnston, 1964), a zone bordering the upper Niagara River was assumed to have a transmissivity of 4.58×10^{-4} m²/sec. This value is about one third the value obtained from the aquifer test analysis yet slightly greater than previously reported values. This value was selected because the aquifer test yielded a local value, whereas the lower value used in the model is more representative of a larger area. Transmissivity is assumed isotropic but nonhomogeneous.

5. Water moves vertically into or out of the Lockport Dolomite through the confining layer.

6. The confining bed is assumed to be 7.6 m thick and is composed of clay and till.

7. The confining-bed hydraulic conductivity is assumed to be 10^{-10} m/sec (Leonard et al., 1977). Because of the better drained soils near the Niagara escarpment (U.S. Department of Agriculture, 1972), this value was increased in that area to 3.28×10^{-9} m/sec. Confining-bed hydraulic conductivity is also isotropic but nonhomogeneous.

8. There are not enough wells reported by Johnston (1964)

to construct a potentiometric surface for the silty sand and silt fill of the shallow system; wells that are in Johnston (1964) indicate that water levels are approximately 3 m below land surface; therefore, values determined from a topographic map were used and 3 m subtracted to produce a shallow-system potentiometric surface. In the Love Canal area, this resulted in heads that were 172 m above mean sea level.

9. The heads in the shallow system represent an average value and neglect seasonal variations or imposed stresses.

10. The rock underlying the permeable part of the dolomite is considered impermeable.

11. The scale of the Lockport Dolomite model is regional, covering most of the area in Figure 8.2.

The area of interest was subdivided into rectangular blocks composing the finite-difference grid shown in Figure 8.3. The grid consists of 21 columns and 23 rows. The northern boundary is considered no-flow because it is located along the middle of a recharge area near the Niagara escarpment, i.e., a ground-water divide. Recharge is through the confining bed. The eastern boundary is approximated as no-flow because it follows a flow line. The southern boundary is treated as constant head and corresponds approximately with the upper Niagara River. The western boundary follows approximately the covered conduits of the pump-storage project and is considered constant head.

Calibration

Calibration of the Lockport Dolomite model consists of matching the observed steady-state potentiometric surface in Figure

8.2. For steady-state flow conditions, the storage term can be eliminated during model calibration. Also, leakage through the confining bed is considered to be under steady-state conditions.

The computed potentiometric surface is shown in Figure 8.4. As may be seen, the match is good on a regional scale, with the hydraulic gradient in the Love Canal area being toward the south and southwest. In terms of spatial distribution, leakage into the Lockport occurred near the topographic high in the northern part of the study area. Leakage out occurred toward the escarpment and at lower elevations toward the upper Niagara River. In the Love Canal area, leakage was generally into the Lockport Dolomite. Thus, in the Love Canal area, the leakage is downward (annually averaged), using the value of 172 m for the head in the shallow system at the Love Canal site. The downward flow in the blocks representing the canal area, however, is very low, with rates ranging from 0.14 to 0.07 mm/yr. The head difference between the dolomite and shallow system is small, especially near the south end of the canal, and, as will be discussed later, the direction of leakage can be easily reversed. As for constant-head nodes, flow was into the dolomite at the pump-storage reservoir and, in general, was out through the western boundary. For the southern boundary, the upper Niagara River was gaining from the dolomite near Love Canal and east; toward the west and near the pump-storage intake, the upper Niagara River was generally losing to the dolomite.

Figure 8.5 shows a comparison of the hydraulic head computed from the steady-state match with the measured values, that is, in just the Love Canal area (section A-A' on Figure 8.4). Even on a local scale, this match is good, with the com-
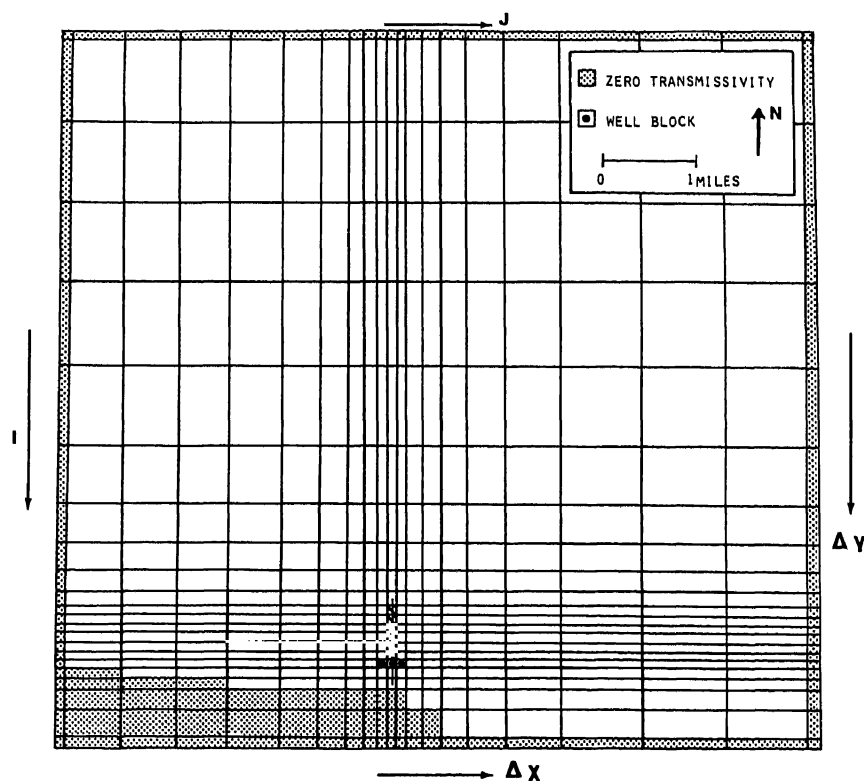
FIGURE 8.3 Finite-difference grid for the Lockport Dolomite model.
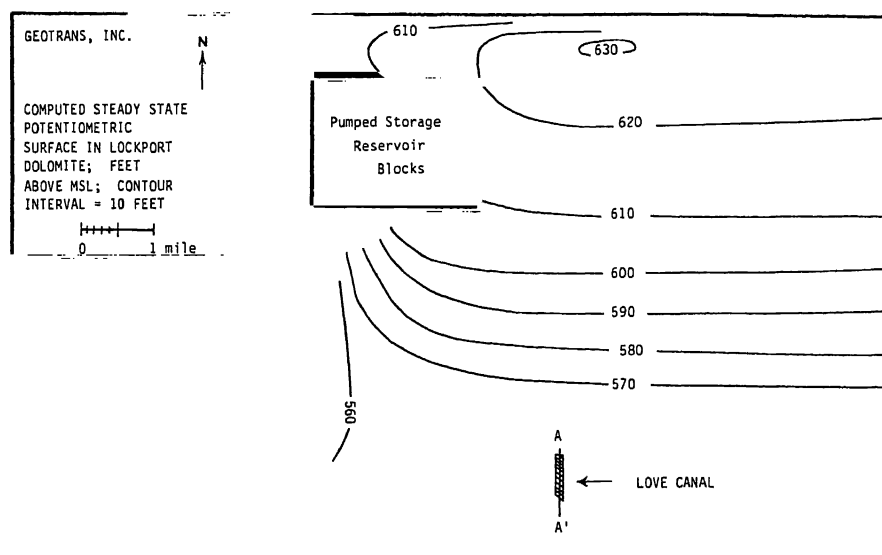
FIGURE 8.4 Computed potentiometric surface for the Lockport Dolomite.

puted values being slightly lower than the observed. This difference may be the result of the head used in the shallow system as well as the constant-head value of 172 m that was used for the upper Niagara River near Love Canal. The observed profile near the river in Figure 8.5 is dashed, indicating that limited data were available there. This also indicates our uncertainty in using 172 m as the constant-head value.

Sensitivity Analysis

A detailed sensitivity analysis was performed on the Lockport Dolomite model. The following were considered: (1) the condition at the western boundary, (2) aquifer transmissivity, (3) confining-bed hydraulic conductivity, (4) river stage at the southern boundary, and (5) water level in the shallow system.
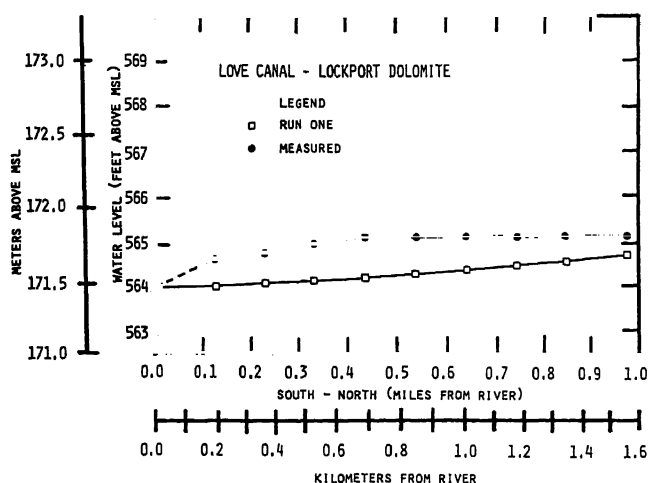
FIGURE 8.5 Magnification of mile 0 to 1.0 (0 to 1.6 km) along section A-A'.

Details are presented in Mercer *et al.* (1981); only the results are presented in Table 8.2.

Predictions Assuming Remedial Action

Under natural conditions, flow in the Lockport Dolomite appears to be at steady state. If remedial action for the dolomite is deemed necessary at some time in the future, the flow field will undoubtedly be disrupted. This will cause transient flow in the dolomite, which can also be simulated.

The steady-state model described in the previous section was modified by varying values for the confining-bed specific storage and the aquifer storage coefficient. For the storage coefficient, a value of 1.5×10^{-4} was used by Mercer *et al.* (1981) as determined from aquifer test analysis. A value of 2.6 $\times 10^{-3}$/m for plastic to stiff clay was estimated for the specific storage of the confining bed (Domenico, 1972). The computed steady-state hydraulic-head distribution in Figure 8.4 was used as the initial condition in the transient model.

If remedial action is necessary for the Lockport Dolomite, installation of interceptor wells is a likely alternative to be considered. To evaluate the effectiveness of this remedial option, interceptor wells were incorporated into the Lockport Dolomite model at the south end of Love Canal. Three wells were placed at the southwest, southcentral, and southeast ends of the canal, since the flow gradient in the Lockport Dolomite is toward the south and southwest. Wells in these locations should intercept any solute that enters the dolomite beneath the canal.

The pumping rates of the three wells were set at 7.6 L/min each. This amounts to a total withdrawal of 32.3 m³/day.

The transient simulation lasted only 6.7 days, after which time the hydraulic heads in the dolomite came to a new steady state. These low pumpages are sufficient to cause a reversal in the hydraulic-head gradient. That is, the flow is no longer toward the upper Niagara River, which means the wells would

TABLE 8.2 Summary of Sensitivity Runs for Dolomite

Run	Description	Effect
1	Lockport Dolomite steady state using constant-head boundary toward the west and best estimate of parameters	"Best" comparison with observed data
2	Same as run 1 except with impermeable boundary toward the west	Minor changes in heads at Love Canal site
3	Same as run 1 with aquifer transmissivity increased by 50%	Slight increase in heads at Love Canal site
4	Same as run 1 with aquifer transmissivity decreased by 50%	Slight decrease in heads at Love Canal site
5	Same as run 1 with confining-bed hydraulic conductivity increased by 50%	Slight decrease in heads at Love Canal site
6	Same as run 1 with confining-bed hydraulic conductivity decreased by 50%	Slight increase in heads at Love Canal site
7	Same as run 1 with river stage increased by 0.3 m	About 1-ft decrease in heads at Love Canal site
8	Same as run 1 with river stage decreased by 0.3 m	About 1-ft decrease in heads at Love Canal site
9	Same as run 1 with heads in the shallow system in the Love Canal area lowered by 0.3 m	Gradients through the confining bed were reversed; flow was out of the dolomite
10	Same as run 1 with confining-bed hydraulic conductivity increased to that of the dolomite in the grid block representing the south end of Love Canal	Created groundwater mound in the dolomite

a well radius of 7.6 cm) would be approximately 0.82 m, so that the assumptions of confined, artesian conditions in the dolomite are still valid.

This new steady-state solution is dependent on the assumption of a constant-head boundary at the upper Niagara River. The hydraulic connection of the river and the Lockport Dolomite is uncertain. If the connection is present to a lesser degree than assumed for the model, then the gradient would still be reversed by this pumpage; however, steady state may not be reached so quickly.

Contamination Travel Times and Uncertainty Analysis

If a contaminant is assumed to have entered the Lockport Dolomite, the travel time for the contaminant to reach the upper Niagara River can be computed. The uncertainty in travel time depends on the accuracy of our knowledge of the hydrogeologic system.

The interstitial velocity of flowing groundwater can be written as

$$v_i = \frac{K}{\phi} \frac{\partial h}{\partial s}, \qquad (8.4)$$

where v_i is the interstitial velocity, K is the hydraulic conductivity, ϕ is the effective porosity, and $\partial h/\partial s$ is the hydraulic gradient. Also note that for convenience the negative sign in Eq. (8.4) has been omitted.

For steady uniform flow, travel time (t) is simply distance (L) divided by interstitial velocity. If all reactions between solute and the rock in which the groundwater is flowing are considered to be simple equilibrium linear sorption reactions, then the amount of solute present on the rock will be directly proportional to the amount of solute present in the fluid. This proportionality constant is the distribution coefficient, k_d, and from it one can calculate the rate of movement of solute in a flowing groundwater system relative to the rate of flow of the transporting water itself according to the expression

$$\frac{\text{water velocity}}{\text{solute velocity}} = \left(1 + \frac{\rho}{\phi} k_d\right), \qquad (8.5)$$

where ρ is the aquifer bulk density.

Adjusting velocities and travel times for this retardation effect results in the following expression for solute travel times:

$$t = \frac{L\phi}{K\left(\dfrac{\partial h}{\partial s}\right)}\left(1 + \frac{\rho}{\phi} k_d\right). \qquad (8.6)$$

Although this is a relatively simple equation, there are considerable uncertainties associated with ϕ, K, and k_d, which lead to uncertainties in the resulting calculated travel times. In this analysis, best estimated travel times to reach surface water for solute with various sorption properties are calculated. The uncertainty of this estimate is evaluated using Monte Carlo simulation techniques. The Monte Carlo approach is used here even though for some of the extreme cases shown a direct analysis can be performed. The direct analysis is discussed later. Note that it is immaterial as to how the contaminant entered the groundwater in the Lockport Dolomite.

The following best estimates are selected for evaluating Eq. (8.6):

$L = 200$ m, distance from the south end of Love Canal to the river;

$K = 3.0 \times 10^{-4}$ m/sec (from aquifer test match, that is, 1.4×10^{-3} m²/sec/4.6 m, where a permeable thickness of 4.6 m is assumed);

$\partial h/\partial s = 1.52 \times 10^{-4}$ (from measured hydraulic head);

$\rho = 2.5$ g/cm³, common limestone density (Clark, 1966);

$\phi = 0.02$, effective porosity (estimated for fractured limestone from Winograd and Thordarson, 1975);

$k_d = 0$ to 10 mL/g (estimated from Apps et al., 1977).

These values are best estimates from observed data, the aquifer-test analysis, and our hydrologic judgment. Eq. (8.6) gives a travel time for a perfect tracer ($k_d = 0$) or for the water itself of 1005 days. That is, if the clays were breached or if solute were transported through the clays, on entering the Lockport Dolomite, it is estimated to take 1005 days for the solute moving with the water to reach the river.

In order to assess the statistical properties in the predicted results, it is first necessary to specify the statistical properties of the uncertain parameters. In this case the parameters in Eq.

(8.6) that have the greatest uncertainty are the hydraulic conductivity, the porosity, and the distribution coefficient. In the following analysis, ϕ and K will be assumed to vary according to specified frequency distributions. Sensitivity analysis may be performed to evaluate the uncertainty in k_d. There is also uncertainty in the simple uniform flow model and in the hydraulic gradient; however, this uncertainty will not be evaluated.

Freeze (1975) presented a large body of both direct and indirect evidence that supports a log-normal frequency distribution for hydraulic conductivity. This distribution refers to the variance of hydraulic conductivity in space. The situation described by Eq. (8.6) is that of a constant, but uncertain, hydraulic conductivity. To evaluate this uncertainty, we assume the same distribution. If the hydraulic conductivity is log-normally distributed, a new parameter $y = \log K$ can be defined that is normally distributed and can be described by a mean value, μ_y, and a standard deviation, σ_y, that is, $N[\mu_y, \sigma_y]$.

For this application, $\mu_y = 1.9365$ and $\sigma_y = 0.5$, that is,

$$K = 0.3 \times 10^{(1.9365 \,\pm\, 0.5)} \text{ m/day}, \qquad (8.7)$$

which is the value obtained from the aquifer-test analysis, with the standard deviation of one-half log unit. Freeze (1975) gives a range of hydraulic conductivity data for fractured rock with standard deviations ranging from 0.20 to 1.56, with a mean of 0.6785. These values of standard deviations indicate a larger spread of values for hydraulic conductivity than that determined from the aquifer test. Because the values in Freeze (1975) are more comprehensive, our value of one-half log unit was estimated from his data. We use feet per day to compute travel times in terms of days.

For the first simulation, Case 1, we estimated porosity to be 2 percent, that is $\phi = 0.02$. Although in theory a value for porosity may be calculated from the storage coefficient obtained from the aquifer tests, in this case it was not possible. The storage coefficient determined from the aquifer test indicates that the aquifer compressibility is more important than the water compressibility. Consequently, the storage coefficient is relatively insensitive to porosity and could not be determined.

Values of K were chosen from a log-normal probability distribution. This was done by recognizing that the values of $y_i = \log K_i$ come from a normal probability distribution. The normal distribution generator is

$$y = \sigma_y S_n + \mu_y, \qquad (8.8)$$

where S_n is a random number taken from a normal distribution with a zero mean and a standard deviation of one, $N[0,1]$. To obtain S_n, we use a random number, R^*_n, uniformly distributed on the interval $(0,1)$. R^*_n is used to compute S_n (also called the random normal deviate, by Ralston and Wilf, 1967):

$$S_n = (-2 \ln R^*_n)^{1/2} \sin 2\pi R^*_{n+1} \qquad (8.9)$$

Using the value of y from Eq. (8.8), hydraulic conductivity is computed from

$$K = 10^y \qquad (8.10)$$

and used in Eq. (8.6) to compute the travel time to the upper Niagara River. To check convergence, we ran the Monte Carlo

simulations for 3200 and 6400 events. No significant difference appeared to exist, and the 6400-event distribution was used.

A plot of the fraction of events in each interval versus the logarithm of travel time for a perfect tracer ($k_d = 0$) is shown in Figure 8.6. Case 1 refers to the case where the "best estimate" for porosity is used. Note that if porosity were decreased by an order of magnitude, the plot would shift one log unit to the left.

The spread of the plotted travel times reflects the confidence with which we are able to specify them, given the precision of our estimate of the hydraulic conductivity, K. A range of 2 standard deviations on each side of the mean encompasses the 95 percent confidence interval. Based on the tabulated mean and standard deviation in Table 8.3, this means that there is a probability of less than 0.05 that the travel time of a tracer (nonretarded element) will be greater than 10,000 days or less than 100 days.

In case 2, we analyze the uncertainty in both hydraulic conductivity and porosity, but assume they are uncorrelated. The same log-normal distribution for hydraulic conductivity is used, but porosity also is assumed log normally distributed with a standard deviation of 0.5 log unit. That is,

$$x = \log \phi, \qquad (8.11)$$

where $N[\mu_x, \sigma_x]$ and $\mu_x = -1.70$ and $\sigma_x = 0.5$. This corresponds to a mean porosity of 0.02. The values of porosity are thus chosen from a log-normal probability distribution, recognizing that the values of $x_i = \log \phi_i$ come from a normal probability distribution. The normal generator is

$$x = \sigma_x S_{n+1} + \mu_x, \qquad (8.12)$$

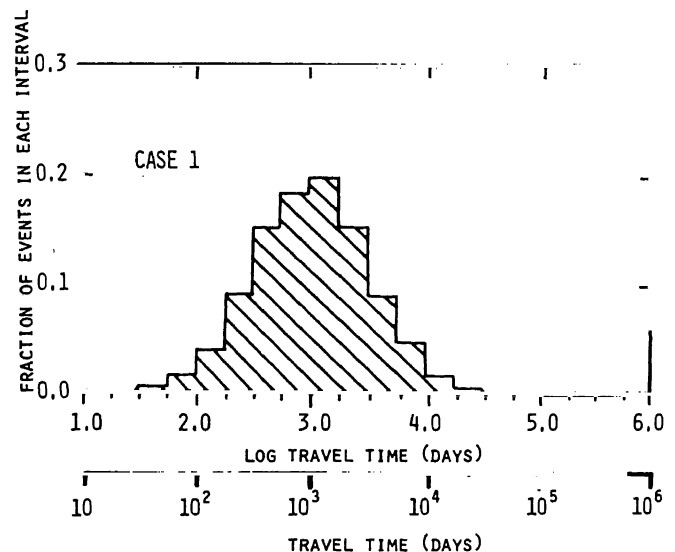where S_{n+1} is a random number taken from $N[0,1]$. S_{n+1} is

FIGURE 8.6 Histogram of travel times in days of solute from the south end of Love Canal to the upper Niagara River through the Lockport Dolomite. Values are computed by Monte Carlo simulation for known porosity, uncertain hydraulic conductivity, and $k_d = 0$.

TABLE 8.3   Value of Log Mean and Log Standard Deviation of Travel Times in Days of Solute from the South End of Love Canal to the Upper Niagara River through the Lockport Dolomite for Several Values of Distribution Coefficients and Varying Uncertainty Assumptions about Hydrologic Parameters[a]

Distribution Coefficient k_d (mL/g)		Monte Carlo		Direct Analysis	
		Case 1	Case 2	Case 1	Case 2
0.0	mean	3.00	3.00	3.00	3.00
	sigma	0.503	0.721	0.5	0.707
0.01	mean	3.35	3.42	—	—
	sigma	0.501	0.545	—	—
0.1	mean	4.13	4.16	4.10	4.10
	sigma	0.502	0.497	0.5	0.5
1.0	mean	5.10	5.10	5.10	5.10
	sigma	0.503	0.502	0.5	0.5
10.0	mean	6.11	6.08	6.10	6.10
	sigma	0.504	0.506	0.5	0.5

[a]Values determined by both Monte Carlo and direct analysis, as shown.

determined from Ralston and Wilf (1967) as

$$S_{n+1} = (-2 \ln R^*_n)^{1/2} \cos 2\pi R^*_{n+1}. \qquad (8.13)$$

Eqs. (8.9) and (8.13) provide a corresponding pair of random normal deviates with zero mean and unit variance for R^*_n and R^*_{n+1}.

Monte Carlo simulations for case 2 are not shown. The most probable travel time again is 3.00 log days, but the standard deviation now is 0.707 log unit. For this case, the probability is less than 0.05 that the travel time of a tracer will be greater than 25,942 days or less than 38 days. This broad spread in travel times in case 2 ($\sigma = 10^{0.707}$) is a result of our assumption that porosity and hydraulic conductivity are completely uncorrelated. There is unquestionably some correlation between porosity and conductivity. However, the amount of correlation is unknown; therefore, there exists uncertainty as to whether the standard deviation of the appropriate travel time is closer to $10^{0.5}$ or $10^{0.707}$. We assume that the travel-time standard deviation is adequately represented by that resulting from uncertainty in the conductivity alone, i.e., $10^{0.5}$, since it is probable that porosity is highly correlated with hydraulic conductivity.

The preceding discussion and the results displayed in Figure 8.6 were restricted to solutes that are not retarded, i.e., to tracers. Such solutes have k_d values of zero, so that the parenthetic expression within Eq. (8.6) equals 1. Many solutes are likely to be retarded, having nonzero k_d values.

To account for retardation, additional sets of Monte Carlo simulations were made using Eq. (8.6) and k_d values of 0.01, 0.1, 1.0, and 10.0. Two runs were made for each k_d value, corresponding to the conductivity and porosity choices of the two cases described above. The results of this sensitivity analysis are given in the form of tabulated log means and standard deviations of travel time in Table 8.3.

The mean values of Table 8.3 show how retardation increases travel time from mean values of $10^{3.00}$ (1000 days) for a tracer to $10^{6.11}$ (1,288,250 days) for a solute with $k_d = 10$. Of particular interest, though, is that the standard deviation associated with

travel times for larger values of k_d is the same and approximately equal to $10^{0.5}$. This follows from direct analysis of the two extreme situations in which $\phi \gg k_d$ and $\phi \ll k_d$. For either extreme, Eq. (8.6) is linear in terms of logarithms. Because it is assumed that K and ϕ are both log normally distributed, the expected value and variance of log t can be calculated directly. Estimates of mean log and log standard deviation of travel time based on direct analysis are also shown in Table 8.3.

Confining Bed

The travel times from the bottom of the canal through the confining bed to the Lockport Dolomite are also of interest. In the calibration of the dolomite model, the leakage rate for a typical block representing the canal was approximately 1.1×10^{-12} m/sec. This value can be used as a basis for estimating travel times through the confining bed by using the formula

$$t = \frac{b'\phi'}{q_z}, \qquad (8.14)$$

where b' is the thickness of the confining bed below the canal, ϕ' is the confining-bed porosity, and q_z is the leakage rate given above.

If it is assumed that the confining bed was not breached during excavation of the canal, there are two extreme possibilities for flow through the confining bed. In the first case, a thickness of 3.0 m for the confining material is assumed. This is less than the 7.6 m used in the dolomite model; however, because we are concerned with the area directly under the canal, it is anticipated that the thickness of the confining bed has been reduced somewhat by excavation. In addition, the confining bed is assumed to have an effective porosity of 0.1. Since we do not know what the effective porosity actually is, the effect of this parameter on the travel time will be demonstrated in the next case. Using these values and the above formula, the travel time for a tracer to reach the dolomite would be about 9000 yr.

Although travel times on the order of thousands of years are

highly likely, a possibility that should not be overlooked is that fissured zones exist in the confining bed. Therefore, in the second case, we assume that the flow through the confining layer is mainly through fractures. This is a clear possibility because fissured clay in the upper shallow sediments in the Love Canal area were described by Owens (1979) and have been reported in other areas with similar geology (Freeze and Cherry, 1979). If fissured, the clay would behave more like a fractured media, and an effective porosity of 0.0001 would be appropriate. Using this value and the 3.0-m thickness, the travel time for a tracer through the confining bed would be about 9 yr. Note that absorption would increase this value.

Of these two extreme cases, the one leading to a longer travel time is more likely. This is because the sediments comprising the confining bed are generally observed to be very moist. The moisture is expected to cause the clay to swell, hence causing the fractures to heal or close. This is supported by Owens (1979), who observed that in the Love Canal area the fissured clays grade to soft moist clays at about 2.7- to 3.4-m depth. In addition, Freeze and Cherry (1979) point out that fracture zones in till and glacio-lacustrine clay tend to be less permeable with depth and that highly fractured zones usually occur only within several meters of the ground surface.

The implication of an expected long travel time through the confining bed is significant. If contamination is found in the Lockport Dolomite, based on the above discussion, four possible explanations, in order of plausibility, are the following:

1. The confining bed was breached during original construction or during modification for disposal;

2. Contamination was caused by leakage from an upper zone because of a poorly sealed well;

3. The confining bed is significantly fractured; or

4. Solvents or some other free-phase organic may have significantly degraded the integrity of the confining bed.

CONCLUSIONS

In many modeling studies, a significant product is the increase in understanding of the hydrologic system. By setting up the model and conducting sensitivity analyses, the investigator gains insight into the behavior of the system and is enabled to make improved predictions of the system's response. This has occurred with the Love Canal study.

As with any modeling study, the worth of the results is dependent on the input. Although there have been numerous studies conducted at Love Canal, the collection of hydrologic data at the canal has been accumulated over only a brief historic interval; therefore, many conclusions must be presented with a note of caution. Reliance on these predictions must be in accordance with the limiting assumptions used in the models. This is not to say that the results and predictions are meaningless. In addition to providing the only means in gaining any understanding of the hydrologic system, the results of modeling can be used to indicate additional data required to improve predictions or strengthen conclusions.

The major conclusions from the Lockport modeling are a mixture of strong supportable conclusions and predictions that require additional data input to gain confidence. Of importance to the Love Canal problem is the potential for contamination of the Lockport Dolomite. This hinges on whether the confining clay beds have been breached under the canal. The vertical Darcian flow velocity through the confining bed is low, with rates on the order of 2.5×10^{-5} m/yr. The direction of flow depends on the local gradient between the shallow system and the dolomite. It could be in either direction, and as the heads fluctuate seasonally, the gradient may reverse. Assuming a downward gradient through the confining bed, and that the confining bed was not breached and does not contain fracture zones, it would take a nonadsorbing solute on the order of hundreds to thousands of years to reach the dolomite. If adsorption occurs, travel times will be even longer. If contaminants traceable to the chemicals disposed in the canal are found in the dolomite, the most likely explanation is that the confining layer was breached, given the long travel times calculated for the confining bed. If the confining beds were breached, downward flow could produce a groundwater high in the dolomite. Since the hydraulic heads in the two systems are nearly equal, however, it is not possible, based on hydrologic evidence alone, to determine whether the confining bed was breached. Thus, additional data would help to resolve this issue. Namely, chemical analyses of Lockport Dolomite groundwater should be obtained to determine if contaminants are present, and longer-term historical data on the head distributions in the shallow and Lockport systems are needed to better identify mounds and gradients between the two systems.

If contaminants were to enter the Lockport Dolomite at the south end of Love Canal, and if there were no adsorption, the mean travel time to the upper Niagara River for the solute would be 1000 days. This is dependent on assumptions concerning the flow properties. Nevertheless, the gradient in the dolomite toward the river may be reversed by placing interceptor wells near the south end of Love Canal. This can be accomplished with a total pumpage as low as 32.3 m³/day.

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Nonpoint Contamination of Groundwater on Long Island, New York

9

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INTRODUCTION

Long Island, New York, lies south of the coast of Connecticut and east of that of New Jersey along the shores of the Atlantic Ocean (Figure 9.1). It has a total area of about 1400 mi² and is 120 mi long by up to 20 mi wide. It includes the counties of Kings and Queens in New York City, which have been population centers for centuries; Nassau County, which grew in population remarkably from the 1940s to about 1970; and Suffolk County, where population growth has been rapid since the 1960s. The island developed slowly for the first three centuries after European settlement in the seventeenth century. The principal use of the land east of New York City was agricultural. Following World War II the rate of suburban development increased, and in this expansion a great deal of farm and estate land changed to housing, light industrial, and commercial development. Today about 8 million people live on Long Island; 3 million in Nassau and Suffolk Counties.

Fresh groundwater stored in unconsolidated sand aquifers underlies virtually the entire island. Kings and part of Queens Counties are supplied with water by sources outside the island, but the remainder of the island relies on this groundwater reservoir. Although an abundant supply of groundwater made development possible anywhere on the island, the effect of discharges in and on the ground has affected the water quality.

This chapter describes the regional contamination of the groundwater supply resulting from the use of the land by all forms of man's activity. Nonpoint contamination is nearly island wide because urbanization and agriculture have both contributed to the problem.

GEOHYDROLOGY

Exploration of the island's water resources began early in this century by Veatch et al. (1906) and Fuller (1914), who described the basic geology and hydrology of the island, and from that time the sources and general movement of the water were known. Most recently the geohydrology of the island was described by McClymonds and Franke (1972). The island consists of a series of beds of sand, silt, and clay dipping somewhat less than 1° toward the south and into the continental shelf. These deposits are underlain by crystalline bedrock of very low permeability. Over most of the island these unconsolidated deposits contain freshwater down to the bedrock. The top of this groundwater reservoir is overlain by glacially related deposits that are mostly of high permeability.

Overall the unconsolidated sediments can be separated into four aquifers and two confining beds (Figure 9.2). The Lloyd aquifer overlies bedrock that is the bottom of the groundwater reservoir. The Lloyd ranges in thickness from about 100 ft in the north to about 400 ft along the southern edge of the island, where it is about 1800 ft below the surface. The Lloyd aquifer is overlain by a confining layer of about 300 ft of silty and solid clay and sand, called the Raritan clay.

The Lloyd aquifer is not extensively used areally but is important for some south-shore communities as it is their only source of freshwater and, being at the bottom of the system, is least altered by contaminants from above. Freshwater is found in the Lloyd throughout the main part of the island; however, freshwater encounters saltwater near the periphery of the island or offshore. The freshwater-saltwater interface
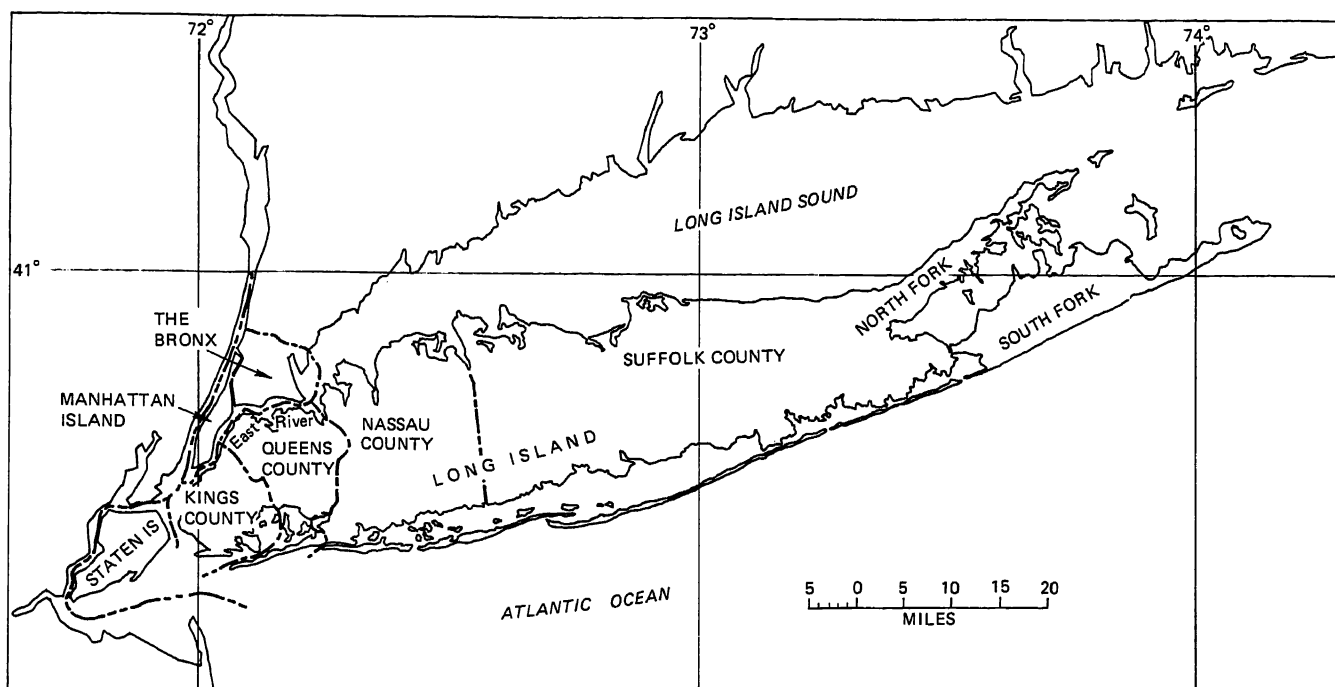
120

FIGURE 9.1 Location and general geographic features of Long Island.

probably follows the north shore of the island where the Lloyd often is in contact with younger, Pleistocene deposits on the updip, eroded edge. The interface on the southern side of the island is seaward of the shore but curves inland in the vicinity of the island's north and south forks.

The Magothy aquifer overlies the Raritan clay confining beds and currently is the most heavily pumped water-bearing unit on the island. It is up to 1000 ft thick along the south shore and about 500 ft thick along the north shore. As the aquifer thickens toward the south shore, the transmissivity in the southern part of the island is about twice that of the northern part. Details of the saltwater-freshwater interface in the Magothy are known only in southeastern Queens and southwestern Nassau Counties, where it is landward of the ocean. In the remainder of the south shore it lies seaward of the barrier beaches (Lusczynski and Swarzenski, 1960). The extent of the part of the fresh groundwater reservoir seaward of the land is unknown and could be sizable. The Jameco aquifer, composed mainly of sand and gravel, overlies the Magothy locally on the west end of the island and along the north shore. It is unimportant regionally but does contain a moving, saltwater wedge (Cohen and Kimmel, 1971).

The Gardiners clay and the 20-ft clay are important confining beds of up to 300 ft in thickness (McClymonds and Franke, 1972) separating the Magothy and Jameco from the overlying upper glacial aquifer along the south part of the island.

The upper glacial aquifer covers the surface of the island and consists largely of those deposits left by the latest episodes of glaciation. It consists of moraine and outwash deposits of sandy, gravelly character.

Fresh groundwater on Long Island originates as precipitation

falling on the island, about half of which percolates through a fairly permeable surface to the water table. Under natural conditions, the reservoir of freshwater underlying the island moves from the water table downward and outward through the reservoir to discharge around the periphery of the island by streams, by subsurface flow into bays and saltwater bodies surrounding the island, and by evaporation. Streams are an important groundwater discharge—about 40 percent of the recharge to groundwater discharges through streams (Cohen *et al.*, 1968). In nonurbanized areas where runoff is not channeled directly into the stream and the water table has not been artificially lowered, about 90 percent of stream flow is derived from groundwater. Consequently, the quality of shallow groundwater in a stream basin is reflected in the base flow of the stream. This feature has been used by some to evaluate the effect of mitigation measures on the water quality.

Beginning in the 1930s stormwater recharge basins were used extensively in Nassau and Suffolk Counties as a measure to facilitate the recharge of water and to dispose of storm runoff. Street runoff is funneled into these basins, where it percolates down to the water table. The infiltration capacity of a basin can be as much as 2 million gallons per day (mgd) (Aronson and Prill, 1977). The effect of these basins on the quality of groundwater has not been studied in detail, but de-icing salts applied to highways and streets must yield some amount of soluble ions such as chloride in the recharge water. Although the danger exists for contamination to enter the groundwater system, the basins have not been found to contribute significantly to pollution. However, they are a significant contribution to groundwater recharge (Seaburn and Aronson, 1974).

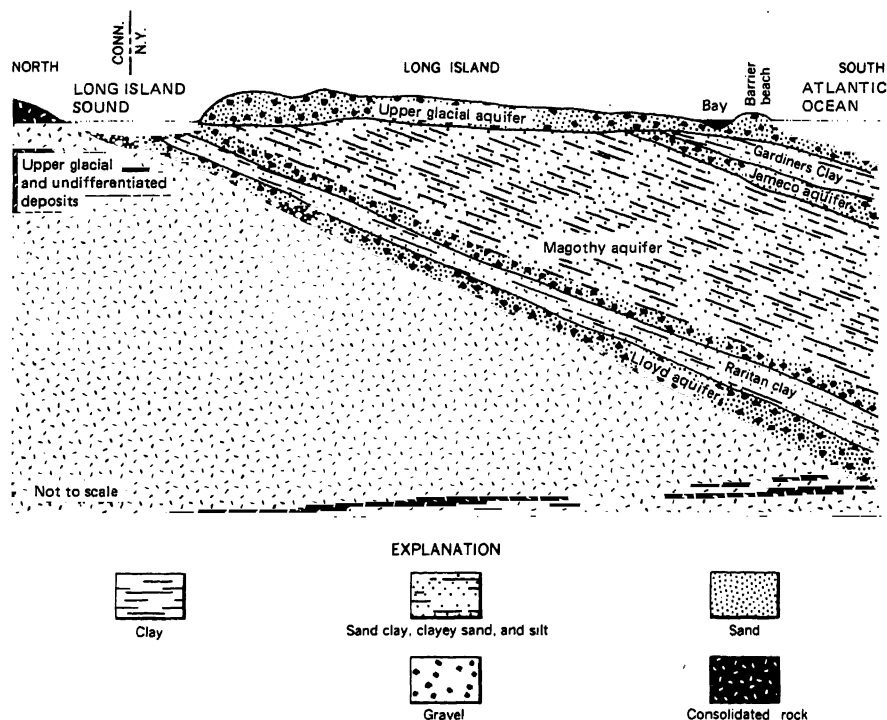Public supply pumpage on Long Island averaged 394 mgd

FIGURE 9.2 Major hydrogeologic units and
flow systems of groundwater reservoirs of Long
Island.

in 1980. About 50 percent of this was from Nassau County, an
area somewhat less than one quarter of the island. Most of the
pumpage is from wells screened from 200 to 600 ft below the
surface in the Magothy aquifer.

Groundwater is the sole source for freshwater in Nassau and
Suffolk Counties and was so designated by the U.S. Environ-
mental Protection Agency (EPA) under Section 1424(e) of the
Safe Drinking Water Act (Public Law 93-523) in June 1978.
Sufficient groundwater is available to meet the needs of Nassau
and Suffolk Counties for the forseeable future, but water quality
will not remain the same for many parts of Long Island (Kop-
pelman, 1978).

NATURAL WATER-QUALITY CONDITIONS

The natural, uncontaminated quality of groundwater on Long
Island can be determined from unsettled areas in the eastern
part of the island and from deep parts of the system where the
age of groundwater is such that contaminants could not have
reached wells and the water does not reflect the activities of
man. Pristine groundwater usually contains less than 50 mg/L
of total dissolved solids (TDS), which change little as water
moves through the system. It also has a low pH and, sometimes,
a bothersome iron content (Franke and McClymonds, 1972, p.
35). Dissolved materials consist mostly of sodium, potassium,
magnesium, chloride, sulfate, carbonate, and bicarbonate. Ni-
trate-nitrogen concentration is less than 0.2 mg/L in uncon-
taminated water (Perlmutter and Koch, 1972). With the ex-

ception of iron, unusual concentrations of heavy metals or other
substances are not known in pristine groundwater.

SALTWATER ENCROACHMENT

When overpumping lowers the hydraulic pressure near the
saltwater-freshwater interface, saltwater is drawn landward. A
well-known example of this occurred in Kings County (Brook-
lyn) between about 1900 and 1947 when overpumping caused
encroachment of salty water. The water table in Kings County
was below sea level in 1936 virtually throughout the county
and dropped to as much as 35 ft below sea level in the northern
part of the county (Lusczynski, 1952). Groundwater encroach-
ment in previous freshwater environments resulted in chloride
and TDS content sufficient to render them unpotable. As other
sources of public water were available for Brooklyn, withdrawal
for public supply ceased.

Public supply pumpage in southern Queens County, which
averages about 60 mgd, continues to cause a sizable, below-
sea-level depression in the water table. Although Soren (1971)
reported some encroachment of freshwater by salty water in
other parts of Queens County, seawater has not been a con-
taminant for these wells. Contamination from above as opposed
to saltwater encroachment from the side has been a major
problem.

In southeastern Queens and southwestern Nassau Counties,
Lusczynski and Swarzenski (1960) defined three wedges of salty
water in the Magothy and above-lying deposits; the deepest of
these lies along the base of the Magothy aquifer and threatens

southwest Nassau County supply wells that are screened near it. However, movement of the entire wedge was not measurable from 1960 to 1969 (Cohen and Kimmel, 1971). The effect of the withdrawal of even 200 mgd in Nassau County produces a very slow movement of the saltwater wedge. This movement will continue as pumpage exceeds recharge.

Further east from the middle of the south shore of Nassau County, the saltwater-freshwater wedge in the Magothy lies offshore. It returns to shore in central Suffolk County, off the Hampton Bay area. In the Lloyd aquifer, the interface is offshore in the southwestern part of the island. In one location on the south shore of Nassau County, salty water has not been encountered after perhaps 40 yr of pumping with hydraulic pressures in the aquifer below sea level. These features suggest that a considerable quantity of fresh, virtually uncontaminable water lies beneath and off the south shore of the central part of the island and could still be considered for development should costs for treatment of contaminated water further into the island become excessive. The full extent of the freshwater south of the island is unknown.

NITRATE

For the most part, surface material on Long Island readily allows the migration of water-soluble products into groundwater. Nitrate is soluble with respect to groundwater and conservative (nonreactive) in regard to sorption. The widespread use of individual waste-disposal systems (e.g., cesspools and septic tanks) on Long Island is the source that is largely responsible for the increase in nitrate content of groundwater. The use of these systems as urbanization spread eastward on the island contributed a major load of nitrate as well as TDS, sulfate, and chloride. Sewerage, which began in Brooklyn about 1850, moved eastward over the island, somewhat behind population growth. Most of Nassau County was only recently sewered after about 30 years of urbanization. In the later part of the 1960s the nitrate content of streams draining urbanized portions of Nassau County contained 14 times more nitrate than urbanized portions of Suffolk County (Koch, 1970).

The earliest source of widespread NO_3 contamination may have been the use of manure fertilizer on farmland in the nineteenth and early twentieth centuries. Nitrogen fertilizers are still an important source of nitrate in groundwater in both urbanized and agriculture areas. Ragone *et al.* (1981) estimated the maximum nonpoint nitrogen load to groundwater in 1975 in Nassau County to be between 10,000 and 10,500 metric tons. A surprising amount of this, 5200 tons, is estimated to come from fertilizers, principally lawn fertilizers; other sources are individual waste-disposal systems, exfiltration from sewers, recharge basins, animal (pet) wastes, rainfall and runoff, landfills, and sewage treatment plants.

Although nitrate from individual waste-disposal systems was found to be a significant source of the total N load in Nassau County, according to Ragone *et al.* (1981, p. 49), fertilizers are the major source in sewered areas. Landfills, a point source, contribute extensive areas of nitrate contamination if located

far enough into the island, and the reduced form of nitrogen, ammonia, is oxidized to nitrate.

Nitrate concentrations greater than 10 mg/L (as N) are considered dangerous to health (U.S. Environmental Protection Agency, 1976); consequently, this forms a basis for rejecting water for potable purposes. In recent years nitrate concentrations greater than this have been found in many parts of Long Island. The depth of nitrate penetration in the aquifer system in Nassau County was examined by Perlmutter and Koch (1972), Ku and Sulam (1976), and Ragone *et al.* (1981). They found alterations of pristine-quality water extending to the base of the Magothy aquifer, some 500 to 600 ft below the surface in the center of the island. Laterally, in the upper glacial aquifer, concentrations of nitrate exceed 10 mg/L in widespread areas of Nassau County. Nitrate contamination follows the regional flow of groundwater in the system and, in the Magothy aquifer, extends about halfway between the central part of the island and the south shore.

Concentrations greater than 6.5 mg/L were found in the upper glacial aquifer in many parts of Suffolk County from 1972 to 1975 (Soren, 1977). Ragone *et al.* (1976a) found significantly elevated nitrate concentrations in water from the deep part of Suffolk County, beginning in the late 1960s.

In Kings County, nitrate occurs in concentrations of over 20 mg/L in widely scattered upper glacial wells. Of 67 analyses of water from the upper glacial aquifer from 1942 to 1971, the mean value of nitrogen was 13 mg/L (Kimmel, 1972). It was concluded that nitrogen came from exfiltration of sewers.

METALS

Analyses of heavy-metal content in Long Island groundwater are not as extensive as those of nitrate. Harr's (1973) sampling of 39 wells in Nassau and Suffolk Counties and Soren's (1977) sampling of 193 wells in Suffolk County are the most extensive studies. Except in areas of point-source contamination, heavy metals have not been found in appreciable amounts. Contamination from metals is not a nonpoint problem. Concentrations of arsenic, barium, cadmium, chromium, lead, mercury, and silver were not found to exceed EPA standards but in some cases may be above that of background concentrations. Copper, which can be dissolved from household plumbing and flushed through septic and cesspool systems, is widespread in urbanized areas but has not been found to exceed 0.5 mg/L in either of the two studies cited.

ORGANIC SOLVENTS

In the mid-1970s additional problems developed as chemical analyses became sensitive enough to identify microgram amounts of organic substances thought to be harmful to human health. By 1979, 37 of 421 public supply wells in Nassau County contained more than 10 μg/L of synthetic organic chemicals (SOC); 23 were closed by New York State Department of Health because the organic chemicals exceeded 50 μg/L, the guideline

for closure of community supplies. By 1979, 500 wells had been tested in Suffolk County; of these, 13 were closed because of SOC (Kim and Stone, 1980).

Tetrachloroethylene, 1,1,2-trichloroethylene, chloroform, 1,1,1-trichloroethane, and carbon tetrachloride were the most commonly found constituents in Long Island water (Kim and Stone, 1980).

In 1980, 13 public supply wells screened in the upper glacial and Magothy aquifers in southeastern Queens County contained SOC; 6 of the 13 were closed. Trichloroethylene and tetrachloroethylene were the main organic chemicals present.

In 1977 a Nassau County Department of Health survey disclosed that at least 292,000 gallons of SOC, principally solvents and cleaning fluids, were used there. Many of these chemicals are deposited directly into individual disposal systems and infiltrate to groundwater. In 1977 about 58 mi^2 of densely populated, unsewered area remained in Nassau County. In that year, the county estimated that 67,500 gallons of cesspool cleaner and the like were sold locally. Evaluation of the cleaner found that over 80 percent was composed of aromatic and halogenated organic solvents. Petroleum distillates make up the remainder of the cleaner.

A survey of the distribution of SOC in the upper glacial aquifer (Koppelman, 1978) found the chemicals widespread. Although this aquifer is little used for public supply, it feeds the Magothy with contaminants as a result of the recharge relation between the upper glacial and Magothy aquifers. Analyses from the county's public supply wells indicate that the distribution of organic contaminants in the Magothy occurs in a wide area in the middle of the county and some locations in north-shore communities.

Past use and disposal of SOC can be expected to cause similar problems in Suffolk County, where sewerage is less extensive.

METHYLENE BLUE ACTIVE SUBSTANCES

A number of studies have documented the presence of methylene blue active substances (MBAS) in the groundwater on Long Island. These chemicals are synthetic detergents added largely through the discharge of individual waste-disposal systems, but leaking sewers and sewage waste disposal in landfills are also contributors. Coin-operated laundries in unsewered areas are large contributors and initially drew attention to the problem. The occurrence of about 1 mg/L of MBAS can cause foaming in water, and for aesthetic reasons a maximum of 0.5 mg/L has been recommended.

Initially, the synthetic detergents industry used alkyl benzene sulfonate (ABS). This compound was found to persist in the environment, which led to the use of biodegradable linear alkyl sulfonate (LAS) in 1965; however, under anerobic conditions, even this compound may persist. Consequently, in 1971 the Suffolk County legislature passed a ban on laundry detergents containing MBAS. In 1981 the ban on laundry detergents in Suffolk County was lifted.

Because of the interconnection between streams and groundwater on Long Island, a shallow subsystem of groundwater flow develops around streams. This subsystem has flushing rates on the order of decades (Franke and Cohen, 1972), and several studies have been made to determine the cleansing action of streams on groundwater.

Koch (1970) analyzed chemical data from the period 1966 through 1969 for streams draining polluted areas of Nassau County and compared them with data from relatively clean areas of Suffolk County. Average MBAS in Nassau County was 0.7 mg/L, while that from Suffolk County was less than 0.1 mg/L—demonstrating how urbanization affected the shallow groundwater quality in Nassau County. Cohen et al. (1971), using data from 1962 to 1969 for Suffolk County streams, found that MBAS content decreased in relation to chloride content and concluded that, in part, this relative decrease may be due to the change in formulation of detergents. From stream-quality data taken between 1961 and 1976, Ragone et al. (1976b) found that MBAS content of streams in Suffolk County was decreasing as a result of the detergent ban, the change in formulation, or both.

Further evidence that efforts to reduce MBAS content of groundwater in Suffolk County were effective was found by Soren (1977). After sampling 171 shallow wells from 1972 to 1975 he noted that concentrations were low (up to 0.15 mg/L) except in the highly urbanized, unsewered southwest part of the county, where the MBAS content was as high as 0.5 mg/L. This area was sewered in the 1970s and should show improvement in the coming decade.

The Long Island comprehensive waste-treatment management plan also found regional decreases in Nassau and Suffolk Counties (Koppelman, 1978). The cleansing action of shallow groundwater by groundwater discharge to streams within the time frame of decades as predicted by Franke and Cohen (1972) apparently is operating, but the complication of a lower water table due to sewerage may prolong the process. Because the streams are largely groundwater fed, a decline in the water table shortens the stream and reduces its discharge.

PESTICIDES

Until 1977 the occurrence of pesticides and herbicide compounds known to have been used on the soil was not found to be a major problem in the groundwater. Harr (1973) in the most extensive survey of pesticides at that time (1972) sampled 10 wells in Nassau and Suffolk Counties and found less than 0.5 µg/L in four wells. In a survey of the shallow groundwater in Suffolk County from 1972 to 1975, Soren (1977, p. 24) found that 15 of 180 well samples contained one or more of DDD, DDE, DDT, diazon, and dieldrin, mostly in amounts less than 0.1 µg/L. The herbicides silvex and 2,4-D were found in even smaller quantities in nine samples.

More recently, Katz and Mallard (1981, p. 179) found dieldrin and heptachlor epoxide and polychlorinated biphenols at concentrations of about 1 µg/L or less at depths of up to 200 ft in central Nassau County.

In 1975 the pesticide aldicarb was introduced in potato fields on the eastern part of the island for control of the potato beetle.

By 1979 the pesticide had reached public water supply wells in one north fork community. In 1980 it was identified in at least 1200 farm and residential wells in the north and south forks. Concentrations of aldicarb in one farm well were as much as 430 μg/L.

CONCLUSION

In summary, the data show that the central part of Long Island has experienced contamination of one sort or another from the surface. Shallow water in this location is critical because it flows down and outward through the groundwater flow system; thus it recharges the deeper aquifers that are the principal water supply for the island. Nitrate and organic chemicals have penetrated deep within the system. Both agricultural practices and urbanization are responsible for this contamination.

In an area where people live on the recharge areas of their water supply it may be impractical to avoid contamination of that supply. Even though the recharge and discharge relations of the groundwater were understood previous to the major development of Nassau and Suffolk Counties, systems of disposal, land use, and pumpage practices were employed that led to the degradation of the water. Though better planning could have reduced this problem, it takes time and research to demonstrate the effect of certain land-use practices. Monetary expenditures are necessary to research and mitigate the contamination, and time is needed to educate people that many of their practices are, indeed, harmful.

So much of the reservoir is contaminated at this time, particularly in the central part of the island, that treatment systems for some water supplies may become necessary. In fact, denitrification is utilized in one water supply. Still, large volumes of uncontaminated water occur in the southern part of the island, which overlies the major part of the groundwater reservoir. This area also is more densely populated. Because the transmissivity is twice as great on the south side than it is on the north side of the island the problem is less dramatic than it otherwise might be, and large supplies may be available from the offshore part of the reservoir. Transfer of water from areas of no contamination is possible should the cost of treatment exceed that of transportation.

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Hydrogeochemical Studies at a Landfill in Delaware

10

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ABSTRACT

Plumes of leachate have migrated downgradient from the Army Creek landfill in Delaware, a site used for disposal of industrial and municipal refuse during the 1960s. A series of contaminant-recovery wells was installed in the early 1970s between the landfill and downgradient water-supply wells to intercept and remove contaminated water. Beneath the landfill and immediately downgradient of the landfill large amounts of iron and manganese are dissolved, organic matter is oxidized and reduced, oxygen is consumed, ammonia is adsorbed, and nitrate is reduced. Farther downgradient some of the reactions are altered: iron and manganese precipitate, less organic matter is oxidized and reduced, and more ammonia is removed by ion exchange. Farther downgradient the water chemistry is controlled largely by mixing. Measurements of chemical constituents in water near the landfill show that most constituents have decreased in concentration over an 8-yr period (1973-1981). As leachate moves downgradient, the attenuation of contaminants is controlled by the following processes: (1) operation of the recovery-well system that removes contaminated water and reverses the local flow, (2) dilution of leachate with native groundwater, (3) mixing of anaerobic leachate with oxygenated water that facilitates the decomposition of organic matter and precipitation of metals, and (4) interaction of contaminants with aquifer materials. Although the recovery-well system has intercepted and removed most of the contaminated water and the quality of water from most downgradient monitor wells has improved, the leachate remains anaerobic, large amounts of gases are generated, and refractory organic compounds are present. Continued pumping of contaminant-recovery wells has lowered the head in the aquifer and wasted a large amount of uncontaminated groundwater.

INTRODUCTION

The movement of contaminated groundwater from waste-disposal sites has become a major problem in many parts of the world. Disposal of liquid and solid wastes in landfills creates an environment where organic and inorganic compounds in the waste or those generated in the landfill are subject to movement in the hydrologic regime. The problems are more pronounced in humid and temperate climates because infiltration of rainfall is high to moderate, and isolation of leachate from the under-

lying aquifers for long periods of time is difficult if not impossible. In these areas landfills become anaerobic and organic materials decay largely through fermentation, thus creating many intermediate organic compounds that affect the groundwater chemistry differently than those originally buried.

The degree to which leachate should be contained, removed and treated, or allowed to move at a controlled rate through natural materials is a basic question that must be considered in making management decisions. In addition to understanding the hydrogeology of an area and the physical processes, such

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as dilution, dispersion, and filtration, an understanding of the biological and geochemical processes is necessary to describe and predict the movement of contaminants. The principal chemical reactions and processes in groundwater at disposal sites include biological decay, precipitation and dissolution of minerals and other inorganic compounds, sorption of chemical constituents, leaching of sediments, ion exchange, generation and diffusion of gases, and movement of dissolved species.

The purposes of this chapter are to review groundwater contamination at a landfill, examine and interpret hydrologic and chemical data available from 1973 to 1981, describe the hydrogeologic processes and chemical reactions that have affected the groundwater chemistry, and discuss the results in terms of long-range planning and management of contaminated aquifers. The landfill studied is the Army Creek landfill, previously known as the Llangollen landfill, in New Castle County, Delaware. Complete chemical analyses for water sampled from the landfill, from immediately downgradient, and from supply-well fields within a mile of the landfill have been published earlier (Baedecker and Back, 1979a, 1979b). Considerable data have been collected by New Castle County and the state of Delaware since 1972 (unpublished files).

The chemical constituents discussed here in detail are Cl^- (because it is considered a conservative parameter), pH, dis- (because it is considered a conservative parameter), pH, dis- carbon, and volatile organic compounds. Except for Cl^- these species are sensitive to oxidation-reduction reactions. The mixing of highly oxygenated groundwater and anaerobic leachate has a significant impact on the water chemistry. Variations in concentrations of chemical species downgradient of the landfill are controlled by changes in leachate composition, changes in the flow path of the leachate, physical attenuation, and chemical reactions.

Statement of Problem

The Army Creek landfill covers about 24 hectares and contains more than 1,500,000 m^3 of refuse. The refuse was deposited from 1960 to 1968 in an abandoned quarry from which 6 to 9 m of sand and gravel had been removed. The excavation con-

tinued until either the water table or a red-clay zone was encountered. Many types of waste were buried, including solid and liquid industrial wastes and municipal refuse. During the 1960s major well fields were developed in a confined aquifer 900 to 1200 m south and east of the landfill. Pumpage from the well fields lowered water levels and increased the downward movement of water from the landfill to the aquifer.

In 1970 the landfill was covered with sandy material and the property was purchased by the county for a park. Two years later a water-quality problem was detected in a nearby domestic well. It was concluded that the absence of or the removal of the red-clay layer in places permitted leachate to migrate into the underlying aquifer (Apgar, 1975). The leachate, highly contaminated in both organic and inorganic compounds, was not adequately diluted or purified by filtration before it entered the aquifer. By 1972, it was confirmed that leachate had spread extensively throughout the confined aquifer and was moving south toward major supply wells.

Description of Site

The Army Creek landfill lies in the Atlantic Coastal Plain and includes both unsaturated and saturated zones. The surficial sands of Pleistocene age, the Columbia Group (Jordan, 1976), are not thick enough in the immediate area to be developed for water supply. Underlying the Columbia sand is the Cretaceous Potomac Formation, which overlies Precambrian rocks. The Potomac Formation consists of silt and clay interbedded with quartz sand and some gravel (Pickett, 1970). The upper sand of the Potomac Formation thickens to the southeast and forms one of the most productive confined aquifers (Potomac aquifer) in the state (Figure 10.1). The upper confining layer (Potomac clay) is thin and may be absent in places close to and beneath the landfill. The major well fields developed in the Potomac sand south and east of the landfill are capable of producing 25 × 10^3 m^3/day of water. Pumping from the well fields has lowered water levels and increased the rate of water movement through the aquifer and increased the downward movement of water from the landfill to the Potomac sand.

To limit the spread of contaminants, a coordinated effort was

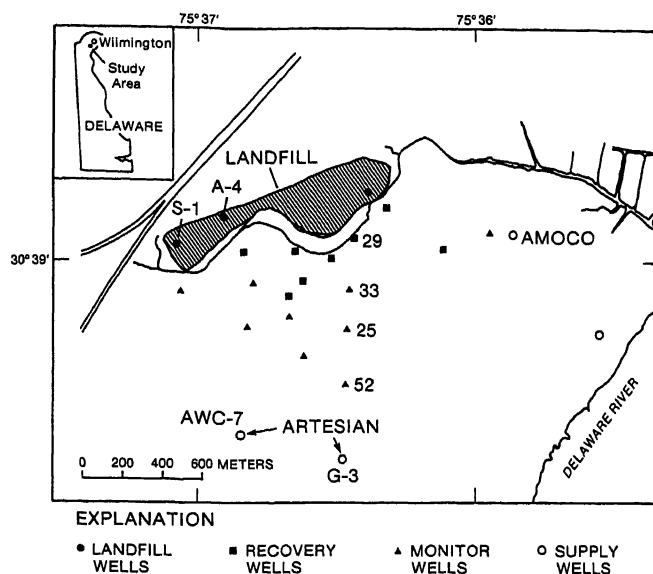FIGURE 10.1 Geohydrologic section of landfill area (from Apgar, 1975).
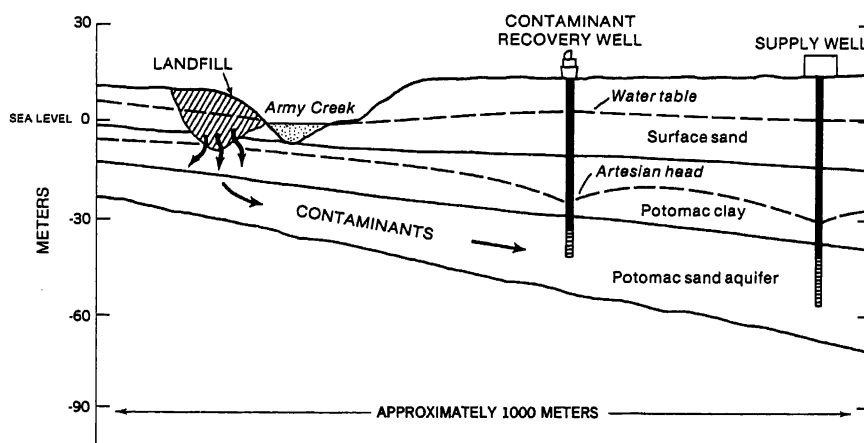
FIGURE 10.2 Location of wells sampled. Wells numbered are referred to in text.

undertaken to reduce pumping from supply wells and to initiate a program of recovery-well pumping between the landfill and the supply wells (Figure 10.2). Pumping of the contaminant-recovery wells caused a local cone of depression, which reduced contaminant movement toward the supply wells. The recovery-well program was begun in 1973 and expanded in 1974 to the 10 wells that operate today, although not all recovery wells have been operating continuously. The recovery wells discharge into Army Creek, which flows into the Delaware River.

The direction of flow in the Potomac aquifer has been altered significantly over the past several decades. Elevation of the potentiometric surface in the 1950s, before significant development of the aquifer, was about 6 m above sea level, and the flow direction was toward Delaware Bay to the southeast. In the 1960s, after well fields were developed for public water supply and industrial use, the direction of flow was to the south and east [Figure 10.3(A)]. The supply wells yield water from the confined sand in the Potomac aquifer from depths of 45 to 60 m. Operation of the recovery-well system reversed the direction of flow locally away from the supply wells [Figure 10.3(B)]. Most of the recovery wells are screened over 12- to 25-m intervals and are completed 25 to 43 m below land surface. The flow pattern indicates that water upgradient from the landfill moves through and beneath the landfill, where it encounters leachate, and is then discharged, in part, by the recovery wells downgradient from the landfill. Part of the discharge from the recovery wells is also native groundwater from south and east of the landfill.

Continued pumping for water supply has permitted contaminants to move south of the recovery-well system [Figure 10.3(C)]. Hydrologic and chemical data indicate that leachate does not migrate at a continuous rate from the landfill but rather moves in pulses. The amount of leachate generated at any one site depends on the amount of recharge to the landfill. It is esti-

mated that 70 percent of the landfill leachate originates as infiltrating percolation on the site, and the remaining 30 percent results from lateral inflow where the refuse is below the water table. These estimates are based on an evaluation of aquifer transmissivity, measurements of the hydraulic gradient in the aquifer adjacent to the landfill, and estimates of rainfall entering the landfill. During periods of low precipitation, the water table declines and less leachate is generated. Another factor that affects the rate of leachate movement in the aquifer is variation in pumpage from wells. Greater pumpage lowers water levels and creates steeper vertical hydraulic gradients from the landfill to the underlying aquifer. The steeper gradients result in more leachate movement into the aquifer and more rapid movement toward the wells.

In 1980 the Amoco chemical plant closed, and its well field 900 m southeast of the landfill was used only for maintenance after 1981. Since then, the direction of groundwater flow is southward [Figure 10.3(D)].

Three major well fields—the county's contaminant recovery system and those operated by the Amoco Chemical Corporation and the Artesian Water Company—account for all pumping in the area. Total pumpage in the immediate vicinity of the landfill has ranged from 20×10^3 m^3/day in 1974 to 12×10^3 m^3/day in 1981 (Figure 10.4). Amoco's pumpage has gradually declined from 5.3×10^3 m^3/day in 1971 to 0.8×10^3 m^3/day in 1981, whereas Artesian's rate reached a maximum of 12.5×10^3 m^3/day in 1972 and a minimum of 5.3×10^3 m^3/day in 1976. The contaminant-recovery-well system was in operation by late 1973 and operated at maximum capacity in 1974 at a withdrawal rate of 9.5×10^3 m^3/day. Since then, pumpage of the recovery wells has declined to an average of 3.8×10^3 m^3/
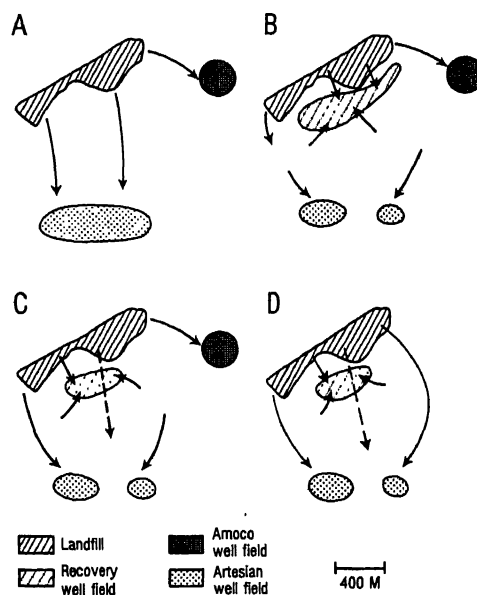
FIGURE 10.3 Schematic of the direction of groundwater flow: A, before the recovery wells were in operation; B, after the recovery wells were in operation; C, after continued pumping for several years; and D, after Amoco well field closed. Dash-lined arrows show movement of contaminants in C and D.
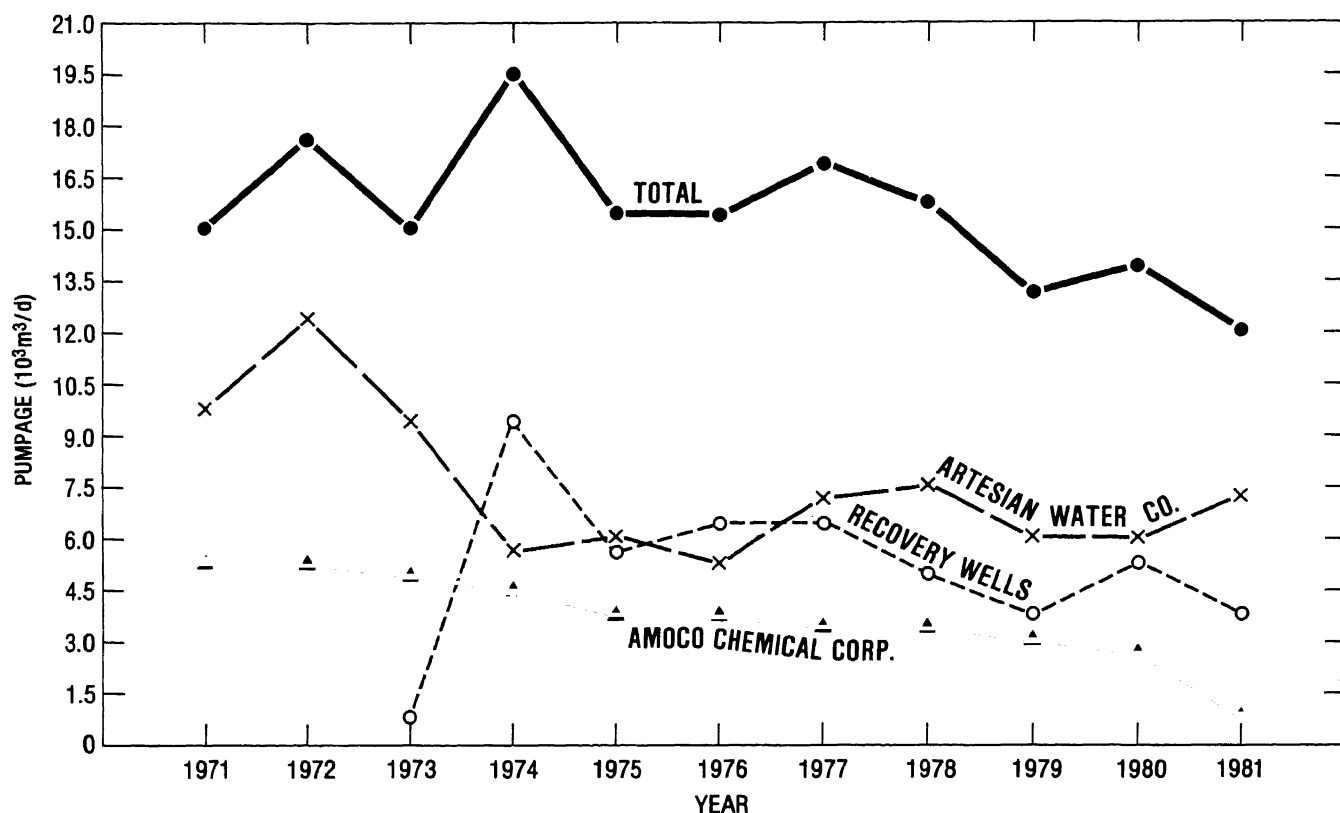
FIGURE 10.4 Pumpage (cubic meters per day) versus time in the immediate vicinity of the landfill.
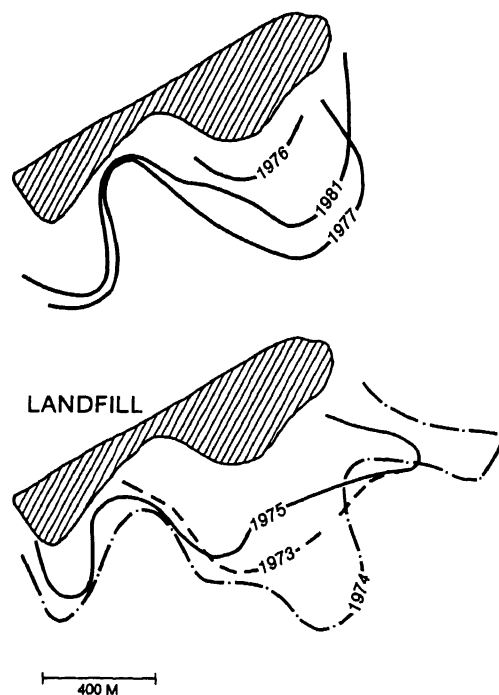
FIGURE 10.5   Lines of equal Cl⁻ concentration (50 mg/L) for the
years 1973 to 1977, and 1981.

day in 1981 because the wells are operating less efficiently and some have been closed permanently.

The location of the wells and their pumpage have influenced the extent of plume migration and concentrations of chemical constituents within the plume, as shown by the 50 mg/L iso-chlor maps for the landfill area (Figure 10.5). The leachate plume migrated significantly farther downgradient in 1974 than in 1973. The effect of the recovery wells in controlling the leachate plume was observed by 1975 and in 1976 when the extent of plume migration was significantly diminished. However, the plume again extended downgradient in 1977 after pumpage of the recovery-well system fell below that of the public water-supply wells (Figure 10.4). Although for the past 5 yr the position of the 50 mg/L isochlor has changed little, the location of the plume and the relative pumpage of the Artesian Water Company and the contaminant-recovery well are in delicate balance.

The distribution of Cl⁻ in the major leachate plume south of the landfill showed the most striking change before 1977 (Figure 10.6). From 1973 to 1976 the concentration of Cl⁻ at recovery-well site 29 decreased from 380 to 50 mg/L. Farther downgradient at well sites 33, 25, and 52, the Cl⁻ concentrations also declined during this time but to a lesser extent. The decline in Cl⁻ concentrations was caused largely by installation of the recovery-well system, which operated most efficiently from 1974 to 1977. Concentrations of Cl⁻ in the water standing
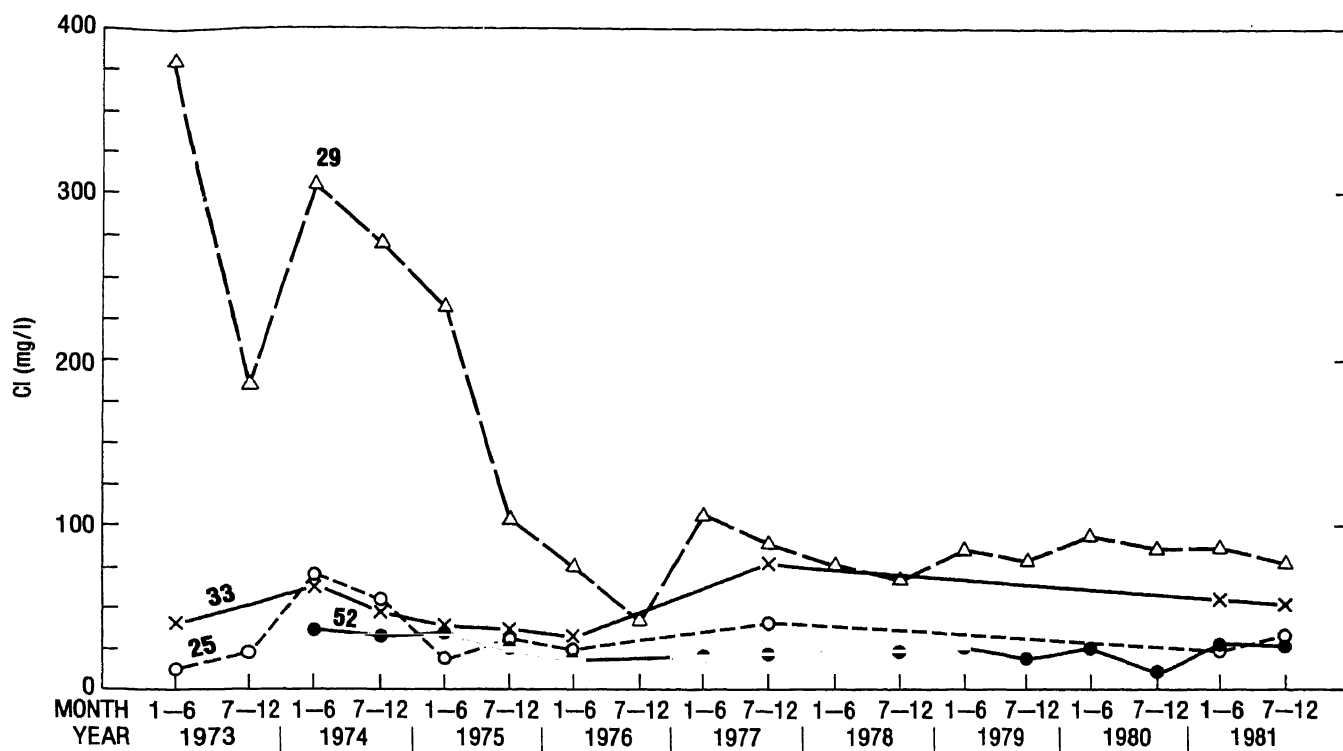
FIGURE 10.6   Average concentration of Cl^- in groundwater from wells 29, 33, 25, and 52 for 1973 to 1981.

in the refuse have declined significantly as a result of previous leaching, and this may, in part, account for the decline down-gradient. In 1977, Cl^- concentrations increased at all sites and since then have remained relatively constant between 25 and 80 mg/L. Pumpage from Artesian Water Company well fields has exceeded pumpage from the contaminant-recovery-well system since 1977.

Alternatives to operation of a recovery-well system to control the generation and movement of leachate were considered by county and state officials for returning the aquifer to full use. Leachate production can be halted only by preventing water from entering the landfill or by removing the refuse. Methods that were evaluated to curtail generation of leachate include covering the landfill with a synthetic surface and isolating the leachate by installation of a barrier or draining ditches. Unfortunately, these solutions are costly and unlikely to eliminate the problem of leachate migration to the aquifer. Removal of the refuse and incinerating it or disposing of it at another site, in addition to being costly, are politically difficult and environmentally disruptive. The cost of isolating the refuse from contact with water was estimated to be in the same range as the cost of moving the landfill. These estimates ranged from $12 million to $16 million in 1974 (Niessen, 1974). To date, installation and operation of the recovery-well system, monitoring groundwater quality, and feasibility studies have cost about $4 million. Surface grading and runoff control could be

used to limit infiltration, although compaction of the refuse and subsidence of cover material are perpetual problems. Some of the recovery wells are currently being relocated on the landfill, which may remove contaminants more efficiently and, in the process, waste less uncontaminated groundwater. The latter remedial measures were estimated in 1978 at $4 million to $6 million in capital and $1 million in annual maintenance costs (Anonymous, 1978).

GEOCHEMICAL ASPECTS

Sampling Techniques

Water samples were collected on the landfill with a metal bailer from 1973 to 1976 and by a peristaltic pump from 1976 to 1981. Monitor wells were sampled with a submersible pump. Recovery and supply wells were sampled at spigots while the wells were pumping. Vandalism and the closing of some recovery wells made it difficult to sample the same wells through the period of study. Wells were pumped or bailed before sampling to remove water standing in the well casing.

Temperature, pH, alkalinity, and dissolved O_2 were measured in the field. A sample was filtered in the field through a 0.45-μm filter for analyses of major anions and cations. Samples for analyses of iron and manganese were filtered through

a 0.1-μm filter to remove colloidal oxidized species. Analyses of CH_4 and organic compounds were made on unfiltered samples. It proved to be difficult to obtain reproducible dissolved organic carbon data because of the high biological activity in leachate-contaminated water. For this study, organic samples were either chilled and analyzed immediately or preserved by the addition of $HgCl_2$ or Ag and chilled until analyzed.

Dissolved Oxygen, pH, and Alkalinity

The concentration of dissolved O_2 ranges from 9.0 mg/L (near saturation) in uncontaminated zones to no detectable O_2 in contaminated water in and near the landfill. The native groundwater is highly oxygenated; however, water moving through the landfill has all of its O_2 removed by respiratory processes. The available oxidizable material in the landfill far exceeds the amount of O_2 in the recharge water. Data from 1977 and 1981 show two major plumes of leachate moving south of the landfill (Figure 10.7). Between the two reducing plumes is a more highly oxygenated area, which has expanded over the 4-yr period. Less contaminated water moves in the aquifer beneath the narrow central part of the landfill, probably because the refuse source is smaller. Also, the aquifer may be thinner or less permeable in this area. Water-level data indicate that the oxygenated area between the reducing plumes may be recharged locally; however, the data are equivocal. The extent of the anaerobic zone southeast of the landfill diminished in 1981 as compared with 1977 as a result of the closing of the Amoco plant well field in 1980.

Large amounts of O_2 are removed from the native groundwater by the oxidation of organic matter and dissolution of metals. In fact, more O_2 than is available in native groundwater is needed to account for the amount of iron precipitated and total inorganic carbon (CO_3^{2-}, HCO_3^-, H_2CO_3) in solution. After all molecular O_2 is utilized, organic matter is both oxidized and reduced by anaerobic fermentative processes to produce CO_2 and reduced organic species, such as CH_4.

The pH of uncontaminated water in the area is between 5.0 and 5.5, which is typical for a poorly buffered water in clay and sand layers that lack calcareous material and are extensively weathered. In contrast, water from the anaerobic zone has a pH between 6.5 and 6.9. Within this zone the pH at any one site has changed little from 1977 to 1981; the average change in pH is 0.09 for five locations for which data are available. The major controls on pH in anaerobic leachate are (1) degradation of organic matter producing large amounts of CO_2, which forms carbonic acid and lowers pH; (2) production of NH_4^+ and CH_4 and reduction of Fe and Mn oxides, all of which consume hydrogen and raise the pH; and (3) exchange of hydrogen on clay, which may lower or raise the pH. Downgradient from the anaerobic zone the pH values of contaminated water range from 5.2 to 6.8. Within this transition zone the average change in pH at each site is 0.26 for the same 4-yr period. The pH varies more in the transition zone because it reflects the subtleties of mixing of the contaminated water with native groundwater.

Measurements of alkalinity in contaminated water consist
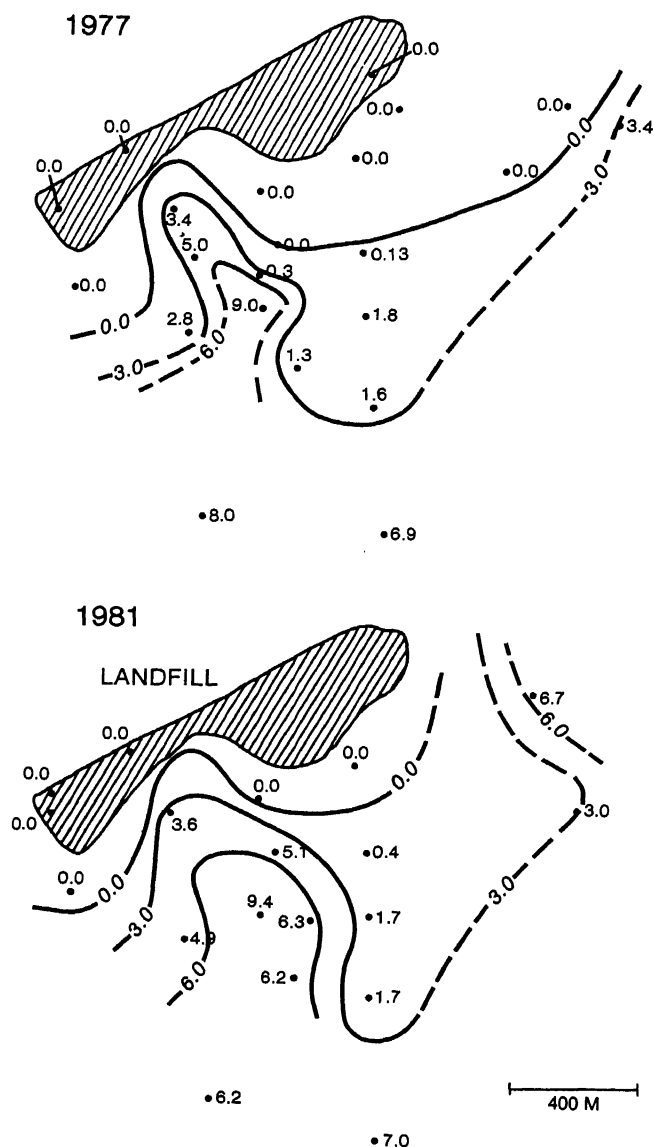
FIGURE 10.7   Distribution of dissolved O_2 in groundwater. Lines of equal concentration drawn for 0.0, 3.0, and 6.0 mg/L.

largely of measurements of HCO_3^-. Although, at some sites on the landfill, organic acids contribute to the total alkalinity, downgradient this contribution is minimal (Baedecker and Back, 1979a). The main control of alkalinity concentration is CO_2 generated from respiratory processes that consume O_2 rather than dissolution of calcareous material. Thus, O_2 is consumed in the landfill, and large amounts of HCO_3^- are generated. As O_2 concentrations increase away from the landfill, HCO_3^- concentrations decrease. The changes in concentrations of O_2 and HCO_3^- due to mixing and chemical reactions are discussed in more detail later.

Uncontaminated oxygenated water (6 mg/L of O_2) has HCO_3^-

concentrations of less than 10 mg/L. Most of the total inorganic carbon (CO_3^{2-}, HCO_3^-, and H_2CO_3) is in the form of carbonic acid (including aqueous CO_2), as reflected in the low pH of the water. Transitional or partially oxygenated water (0.3 to 6.0 mg/L of O_2) has HCO_3^- concentrations between 12 and 75 mg/L, whereas anoxic water has HCO_3^- concentrations of >100 mg/L. With a few exceptions, alkalinity concentrations changed little from 1977 to 1981. The largest change was a decrease in alkalinity at site S-1 on the landfill, a site that has consistently produced the most concentrated leachate. Previous results showed that a large part of the alkalinity at site S-1 was organic acid anions rather than from HCO_3^-. More recently, the contribution from organic acids has greatly decreased, and this may, in part, account for the decrease in alkalinity from 4450 mg/L to 1570 mg/L over the 4-yr period.

Major Constituents

The relative abundances of the major inorganic constituents in water, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, NO_3^-, and SO_4^{2-}, are significantly different in the anaerobic zone and the native groundwater. The average concentrations as percentage of milliequivalents/liter (meq/L) and standard deviation of major inorganic constituents are shown in Figure 10.8 for three water types, based on dissolved O_2 concentrations. Native groundwater unaffected by leachate is shown in group A as a Ca-Mg type with Cl^- as the major anion. Sulfate concentrations are quite low in both the leachate and natural water. Rainfall is the major source of Cl^- in the native groundwater; rainfall and oxidation of iron sulfide are the main sources of SO_4^{2-}. Concentrations of all constituents are quite low in the natural water, which has dissolved solids (DS) of 50 to 90 mg/L. This mixed-cation type of water, in which no cation contributes more than 50 percent to total cations, is characteristic of much water in recharge areas of the Atlantic Coastal Plain.

Group C, the anaerobic zone, includes those samples from the landfill and the recovery wells immediately downgradient. This water is a sodium bicarbonate type, and in 1981 the DS ranged from 250 to 2000 mg/L. During 1977 to 1981 the DS at S-1 showed the most significant change from 6400 mg/L in 1977 to 2000 mg/L in 1981. This is consistent with other data that show that the concentrations of all constituents in the leachate at S-1 have decreased. Other sites within this zone have DS values that were lower from 1977 to 1981 by about 16 percent. Concentrations of constituents other than those shown in Figure 10.8, including NH_4^+, Fe^{2+}, Mn^{2+}, CH_4, and organic compounds, are high in this water type. In fact, NH_4^+ and Fe^{2+} account for 14 to 50 percent of the total cations in the anaerobic zone. The high values of HCO_3^-, CH_4, and NH_4^+ result from degradation of organic matter by fermentation.

A major source of cations (Mg^{2+}, Ca^{2+}, Na^+, K^+) may be their exchange from clays by NH_4^+ generated in the leachate. The high concentrations of Fe^{2+} and Mn^{2+} most likely result from their mobilization when water, which has a reducing potential due to the presence of organic material, comes in contact

Percent of Constituents
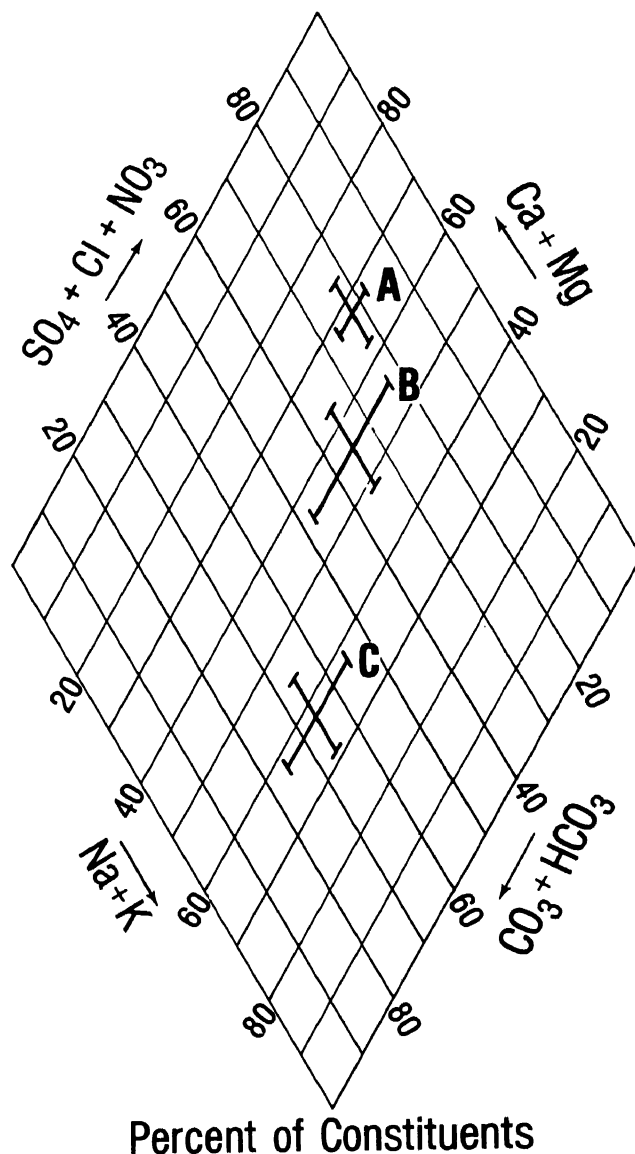
FIGURE 10.8 Inorganic chemical composition of groundwater for (A) the native groundwater, high in O_2; (B) transition zone, low in O_2; and (C) the anoxic zone. Average concentrations and standard deviation in percentage of total milliequivalents per liter for cations and anions (modified from Baedecker and Back, 1979a).

either with metals in the refuse or with oxidized Mn-bearing minerals and ferric oxide cements in the sand and clay.

Water in the transition zone (B) is intermediate between water types A and C and is a mixed cation-anion type. The water chemistry in this zone results largely from mixing of leachate with native groundwater, with only minor changes as a result of chemical reactions. The values for DS in this zone ranged from 50 to 160 mg/L in 1981, which is about 30 percent lower than those measured in 1977.

Organic Compounds

Organic carbon concentrations in the landfill ranged from 77 to 260 mg/L in 1981. A marked decline was observed at landfill site S-1 from 3700 mg/L in 1977 to 260 mg/L in 1981. Organic carbon concentrations decrease rapidly downgradient from the landfill to low values of <0.1 mg/L in uncontaminated water (Table 10.1). Organic carbon concentrations vary more with time and sampling procedures than concentrations of inorganic constituents. Much of the organic matter is oxidized as the leachate migrates, and some is adsorbed on mineral surfaces. Sorption is expected to be greater if sediments in contact with the water have a high organic content and if the compounds sorbed have low solubilities and polar functional groups (Griffin and Chian, 1979; Means *et al.*, 1980). Although the clay is weathered and the organic material is low, some lignitic silt was found in Potomac Formation cuttings when the wells were installed. Many of the organic compounds in the water are polar, such as organic acids and chlorinated compounds, and may sorb more readily on sediments. Because organic acids are highly reactive, they disappear rapidly downgradient. By contrast, the chlorinated hydrocarbons are more refractory and may persist for a long time.

Volatile organic compounds (VOC) were identified in the water samples by purging the water with inert gas, trapping the compounds on a Tenax column, and eluting them into a gas chromatography-mass spectrometry system (Pereira and Hughes, 1980). The compounds with confirmed identification, that is, analyzed with standards run under the same conditions, are listed in Table 10.1. The column 3 (total VOC) is the sum of all compounds identified, including those for which identification is tentative. Aromatic hydrocarbons are the most prevalent of the compounds definitely identified. The same compounds are not present throughout the landfill, as shown by comparison of analyses from sites A-4 and S-1. The total concentration of VOC decreases rapidly away from the landfill and

recovery wells but does not drop much below 10 μg/L. In an earlier study of VOC in the landfill area by DeWalle and Chian (1980), S-1 reportedly had a much higher concentration of VOC (982,000 μg/L) compared with recent values (840 μg/L) reported here. Although it is difficult to compare analyses from different laboratories, concentrations of VOC in water collected in 1981 are significantly lower than those in water collected in 1977 for the study by DeWalle and Chian. Another factor that may have affected the concentration of VOC is lowering of the water table at site S-1, which was 5 m below land surface in June 1981 as compared with previous water depths of 3.6 m. As a result, a much smaller volume of refuse was saturated in 1981. The lower values for specific organic compounds in the landfill leachate and the water downgradient over a 4-yr period are consistent with lower total organic carbon values and suggest that organic compounds are being removed from the aquifer.

High concentrations of CH_4 in the landfill result from microbial degradation under anoxic conditions. CH_4 concentrations have decreased from 22 mg/L in 1977 to 14 mg/L in 1981 in water collected at site A-4 in the landfill. However, at site S-1, which is located in the newest part of the landfill, CH_4 concentrations have increased from 10 mg/L in 1977 to >20 mg/L in 1981. This difference may indicate that the newer part of the landfill near S-1 may have reached the state of high CH_4 production at a later time than the zone near A-4. Nicholson *et al.* (in press) have shown that the gas initially produced in landfills is predominantly CO_2, whereas at later stages the predominant gas is CH_4. Expressed in partial pressures, CH_4 concentration of 20 mg/L is about 0.74 atm at 16°C, which means it constitutes 74 percent of the total gases in solution and is probably near maximum concentration. Concentrations of CH_4 decrease rapidly downgradient and are below the limit of detection in the supply wells. However, CH_4 has continued to move downgradient and is present in water containing as much as 1.7 mg/L of O_2.

TABLE 10.1   Dissolved Organic Carbon and Volatile Organic Compounds (VOC) in Groundwater at Army Creek Landfill

Wells	DOC (mg/L)	Total VOC (μg/L)	Number of Compounds	VOC (μg/L) Methylene Chloride	Benzene	Toluene	Ethyl Benzene	Chloro- benzene	Trichloro- ethene	Ethane[a] Dioic Acid
Landfill										
S-1	260	843.5	26	—	76.8	3.0	35.0	—	—	224.7
A-4	77	843.0	34	3.7	140.0	0.7	92.8	16.1	—	207.7
Monitor/Recovery										
29	13	242.4	21	1.8	6.9	0.1	0.4	19.5	—	—
33	3.4	29.8	18	—	2.2	—	—	1.3[a]	0.2	3.1
25	2.7	26.7	13	—	2.3	—	—	1.6[a]	—	—
52	1.0	15.4	11	2.4	0.4	—	—	—	0.2	—
Supply										
G-3	0.1	18.4	7	7.2	—	—	—	—	—	—
AWC-7	0.1	8.9	10	—	—	—	—	—	—	—

[a]Identification tentative.

move downgradient and is present in water containing as much as 1.7 mg/L of O_2.

Chemical Mass Balance

Although most of the leachate is removed downgradient by the recovery wells, some contaminated water travels beyond the recovery-well system, and the behavior and fate of this water with its constituents are considered in more detail. The contaminants are attenuated by mixing, by chemical reactions, and by physical processes as the leachate moves downgradient. The controlling reactions and processes that alter the chemical composition of leachate as it moves along a groundwater-flow path were simulated by a chemical mass-balance model. The first calculation in the model is to evaluate the role of mixing of the contaminated water with native groundwater. The second calculation is to simulate chemical reactions to generate a chemical composition of water identical to that obtained by chemical analyses. Chemical modeling identifies a set of plausible chemical reactions but does not provide a unique set of chemical reactions.

The extent of attenuation by mixing was calculated using Cl^- as a conservative parameter. The flow path of contaminants, based on the distribution of chemical species, is from the landfill to well 29 and between the following wells: 29 to 33, 33 to 25, and 25 to 52 (Figure 10.2). Site A-4 was used as the leachate end member because its water chemistry has been relatively consistent over a 5-yr period and because in recent years the wells have been destroyed on the eastern part of the landfill and recent data are not available. Chemistry of the native groundwater, the other end member, is based on the analyses of water from uncontaminated supply wells. Ratios of the mixing components were determined by assuming that Cl^- concentrations along the path are controlled only by mixing of contaminated water with native groundwater. For other constituents, deviations of observed concentrations from those calculated by using the mixing ratios represent an enrichment or depletion of species due to chemical reactions or processes. It must be assumed that the concentrations of constituents have been constant at any one point along the flow path during the time required for water from the landfill to reach the outermost well. The flow time was estimated to be 2 yr.

This discussion is limited to abundances of species that are related to the presence of organic matter and that are sensitive to the availability of O_2 and therefore subject to oxidation-reduction processes. To construct a model to explain the sources and sinks of constituents, limitations were placed on the possible reactions, which are given in Table 10.2. For example, sources of Fe and Mn were limited to natural oxide coatings, Fe_2O_3 or MnO_2, even though another possible source is the material deposited within the landfill. In the model, Mn^{2+} was precipitated as MnO_2 or $MnCO_3$, and Fe^{2+} was precipitated either as $Fe(OH)_3$ or $FeCO_3$, depending on saturation values at each site. NO_3^- was reduced to N_2, although it can be reduced to either N_2O or NH_4^+ under certain conditions. Because nitrification does not occur in the anaerobic water, NH_4^+ was removed by cation exchange on clay. Organic matter of the composition CH_2O was oxidized to CO_2; and organic matter

TABLE 10.2 Chemical Reactions Used in Model

(1)	$Fe_2O_3 + 2H^+ + CH_2O \rightarrow 2Fe^{2+} + 2H_2O + CO_2$
(2)	$2MnO_2 + 4H^+ + CH_2O \rightarrow 2Mn^{2+} + 3H_2O + CO_2$
(3)	$Fe^{2+} + 2HCO_3^- \rightarrow FeCO_3 + H_2CO_3$
(4)	$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$
(5)	$2Mn^{2+} + O_2 + 2H_2O \rightarrow 2MnO_2 + 4H^+$
(6)	$4NO_3^- + 5CH_2O \rightarrow 5CO_2 + 3H_2O + 4OH^- + 2N_2$
(7)	$CH_2O + O_2 \rightarrow CO_2 + H_2O$
(8)	$C_8NH_{17}O_8 + 2H_2O \rightarrow NH_3 + 2C_2H_6O + 4CO_2 + 3H_2$
(9)	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
(10)	$Cation\text{-}clay + NH_4^+ \rightarrow NH_4^+\text{-}clay + cation$

containing nitrogen, represented in a general formula by $C_8NH_{17}O_8$, was oxidized to CO_2, reduced to NH_4^+, and partially reduced to C_2H_6O. Several pathways are known for the formation of CH_4, such as via an acetate intermediate; however, for this model CH_4 was formed by the hydrogenation of CO_2. Although the stoichiometry assigned to organic matter is not unequivocal, it is consistent with reactions known to occur in anaerobic environments. CH_2O is an oxidized form of organic material as in carbohydrates, $C_8NH_{17}O_8$ is an oxidized form of organic material with an C:N ratio of 8:1, and C_2H_6O is a partially reduced form of organic material as in alcohols.

After the mixing ratios were determined, the amounts of reactants and products in the reactions were calculated using, in part, the computer program BALANCE (Parkhurst et al., 1982). Electrons were balanced, but the concentrations of H^+ and OH^- were not calculated because they are components of water. Thus, the sequence of mass-balance calculations for each step along the flow path is as follows:

Chemical composition of water at Point A

$\downarrow$

$$\begin{bmatrix} \text{Chemical composition} & \text{Gain or loss} \\ \text{of water after mixing} & \text{of species due} \\ \text{water from Point A} & + & \text{to chemical} \\ \text{with native} & \text{reactions} \\ \text{groundwater} & \text{(Table 10.2)} \end{bmatrix}$$

$\downarrow$

Chemical composition of water at Point B

The chemical compositions of water at Points A and B were determined analytically, and the chemical composition of water after mixing was calculated from mixing ratios. Finally, the amounts of reactants and products for the chemical reactions were calculated to balance the abundances of species.

In the first step (Table 10.3, Part A), the concentrations of dissolved constitutents in the leachate are altered by mixing 21.9 percent leachate from well A-4 with 78.1 percent native groundwater. The concentrations of all constituents decrease with the exception of O_2 and NO_3^-, which increase because these constituents are higher in the native groundwater than in the landfill water. The results of the chemical mass balance show that from the landfill (A-4) to the recovery well (29) iron and manganese oxides dissolve, organic matter is oxidized and reduced, O_2 is consumed, NH_4^+ is exchanged, and NO_3^- is

TABLE 10.3 Chemical Mass Balance along Flowpath at Army Creek Landfill (mmoles/L)

A. Species	Water at Well A-4	After Mixing [a]	Chemical Reactions	Water at Well 29
ΣCO_2	26.59	6.95	0.274 Fe_2O_3 dissolves	10.12
CH_4	0.875	0.192	0.020 MnO_2 dissolves	0.256
NO_3^-	0.029	0.054	0.261 O_2 consumed	0.027
NH_4^+	8.150 → 1.788	+	0.655 $C_8NH_{17}O_8$ consumed	→ 2.445
Fe^{2+}	0.269	0.062	0.612 CH_2O consumed	0.609
Mn^{2+}	0.002	0.0005	0.002 NH_4^+ exchanges	0.020
O_2	0.0	0.261	1.310 C_2H_6O generated	0.0
Cl^-	9.027	2.20	0.027 N_2 generated	2.20
			1.709 H_2 generated	

[a] 21.9% Well A-4 Water + 78.1% NGW.

B. Species	Water at Well 29	After Mixing [b]	Chemical Reactions	Water at Well 33
ΣCO_2	10.29	6.41	0.130 O_2 consumed	4.45
CH_4	0.256	0.147	0.179 CH_2O consumed	0.034
NO_3^-	0.027	0.042	1.266 NH_4^+ exchanges	0.003
NH_4^+	2.445 → 1.402	+	0.350 $FeCO_3$ ppt	→ 0.136
Fe^{2+}	0.609	0.351	0.010 MnO_2 ppt	0.0009
Mn^{2+}	0.020	0.012	0.020 N_2 generated	0.0015
O_2	0.0	0.143	1.78 CO_2 outgasses	0.013
Cl^-	2.20	1.38	0.113 CH_4 outgasses	1.38

[b] 57.4% Well 29 Water + 42.6% NGW.

C. Species	Water at Well 33	After Mixing [c]	Chemical Reactions	Water at Well 25
ΣCO_2	4.45	3.44	0.0006 MnO_2 dissolves	3.28
CH_4	0.034	0.023	0.067 O_2 consumed	0.007
NO_3^-	0.003	0.023	0.089 CH_2O consumed	0.003
NH_4^+	0.136 → 0.091	+	0.077 NH_4^+ exchanges	→ 0.014
Fe^{2+}	0.001	0.0016	0.0012 $Fe(OH)_3$ ppt	0.0004
Mn^{2+}	0.001	0.0011	0.011 N_2 generated	0.0017
O_2	0.013	0.120	0.016 CH_4 outgasses	0.053
Cl^-	1.38	1.02	0.25 CO_2 outgasses	1.02

[c] 66.7% Well 33 Water + 33.3% NGW.

D. Species	Water at Well 25	After Mixing [d]	Chemical Reactions	Water at Well 52
ΣCO_2	3.28	2.49	0.119 O_2 consumed	2.23
CH_4	0.007	0.004	0.127 CH_2O consumed	0.038
NO_3^-	0.003	0.028	0.008 NH_4^+ exchanges	0.021
NH_4^+	0.014 → 0.008	+	0.0006 $Fe(OH)_3$ ppt	→ 0.00
Fe^{2+}	0.0004	0.0015	0.0009 MnO_2 ppt	0.0009
Mn^{2+}	0.0017	0.0011	0.004 N_2 generated	0.0002
O_2	0.053	0.172	0.35 CO_2 outgasses	0.053
Cl^-	1.02	0.65		0.65

[d] 57.7% Well 25 Water + 42.3% NGW.

NOTE: Native groundwater (NGW) composition: ΣCO_2 = 1.43; CH_4 = 0.0; NO_3^- = 0.0613; NH_4^+ = 0.0; Fe^{2+} = 0.031; Mn^{2+} = 0.0002; O_2 = 0.3344; Cl^- = 0.28.

reduced. As a result of these processes, water of the chemical composition found at well 29 is simulated. In addition, a partially reduced form of organic matter (C_2H_6O), N_2, and H_2 is generated. The dissolution of Fe_2O_3 and MnO_2 by reactions (1) and (2) (Table 10.2) and reduction of NO_3^- by reaction (6) produce 0.35 mmole/L of ΣCO_2 of which 0.06 mmole/L was used to form CH_4.

The limit on the amount of organic matter oxidized by reaction (7) is the amount of O_2 that needs to be removed from solution, whereas the amount of organic matter used by reaction (8) is controlled by the amount of CO_2 needed at site 29 in addition to that produced by the reactions discussed above. These reactions [(7) and (8)] produce another 2.62 mmoles/ L of CO_2. Of the total amount of H_2 produced, a small portion, 0.26 mmole/L, is used to form CH_4, which leaves 1.71 mmoles/ L of H_2. Because H_2 was not found in the gases it was probably removed from solution by organic reactions such as C_nH_{2n} + removed from solution by organic reactions such as C_nH_{2n} + was outgassed. In the above reaction, where $n = 2$, C_2H_4 (ethylene) would be hydrogenated to C_2H_6 (ethane), both of these compounds were identified in the leachate. However, it is equally probable that CH_4 is formed and subsequently outgassed. On the landfill, significant quantities of CH_4 can escape and O_2 can be replenished before the leachate reaches the confined aquifer. This also means that more organic matter can be oxidized than is indicated in the model as long as the products outgas. The nitrogen in the organic matter is reduced, forming NH_4^+. Most of the NH_4^+ remains in solution, and the excess of the mass balance is exchanged on clay.

The reactions in the next sequential step downgradient be-tween well 29 and well 33 are significantly different from those discussed above. In this step (Table 10.3, Part B), the concentrations of dissolved constituents are altered by mixing 57.4 percent water from well 29 with 42.6 percent native groundwater. In contrast to the previous step, ΣCO_2, CH_4, Fe^{2+}, and Mn^{2+} are in excess in the mixed water and must be removed. Fe^{2+} precipitates as $FeCO_3$, Mn^{2+} as MnO_2, and CO_2 and CH_4 outgas. As in the previous step, NH_4^+ and O_2 are removed by ion exchange and oxidative processes, respectively. It is necessary to oxidize only 0.18 mmole/L of organic matter to simulate the water chemistry; however, these reactions are difficult to quantify, and, as discussed above, it is possible that more organic matter is oxidized and reduced and the end products (CO_2 and CH_4) outgas. Because the confining layer is thin close to the landfill and the partial pressures of CO_2 and CH_4 are high, outgassing is possible in this part of the aquifer. Iron precipitates as either siderite or amorphous iron oxide based on thermodynamic saturation data calculated by the chemical equilibria computer program WATEQF (Plummer et al., 1976). The saturation index [log (ion activity product/equilibrium constant)] is 0.97 for siderite and 1.43 for amorphous iron oxide. However, siderite is more stable than amorphous iron oxide under these conditions, with a pH of 6.6, calculated Eh of approximately 0.2 V, ΣCO_2 concentration of 10^{-2} mole, and Fe concentration of 10^{-4} mole.

In the next step (Table 10.3, Part C), the concentrations of dissolved constituents are altered by mixing 66.7 percent of water from well 33 with 33.3 percent native groundwater. Likewise, for the following step (Table 10.3, Part D), 57.7 percent of water from well 25 is mixed with 42.3 percent native ground-

r. In these steps, from well 33 to well 25, and well 25 to the water chemistry is simulated largely by mixing. In rast to the sites upgradient, little NH_4^+ is exchanged, less ; removed, and little solution or precipitation of minerals rs. The amounts of Fe^{2+} and Mn^{2+} transferred (0.001)le/L) are low and close to the limits of precision of the rminations. Small amounts of organic matter are oxidized, 0.2 to 0.4 mmole/L of CO_2 outgasses. It is unlikely that would outgas through a confining layer of this thickness ·e than 30 m), even though the P_{CO_2}s of water (0.05 atm at 25 and 0.04 atm at 52) are greater than P_{CO_2} of the atmo-:re. Also, the model shows that CH_4 was generated be-:n sites 25 and 52, which is not possible in the presence cygen.

possible explanation is that CO_2 and CH_4 concentrations licted by mixing are not valid at these sites and that gases present in solution from an earlier reducing front that ex-led downgradient. Alternatively, a microreducing environ-ıt may exist that permits gases to be generated in the aqui-Less CO_2 is generated by considering other equations for oxidation of organic matter. Reaction (7) (Table 10.2) uses ;O as a form of organic material, whereas using a more ıced form of organic material such as C_2H_6O or CH_4 yields CO_2 for the same amount of O_2 consumed. This is shown :he following equations, in decreasing oxidation state of ınic compounds:

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O \quad [O_2/CO_2 = 1] \quad (10.1)$$
$$C_2H_6O + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad [O_2/CO_2 = 1.5] \quad (10.2)$$
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad [O_2/CO_2 = 2] \quad (10.3)$$
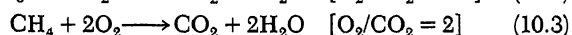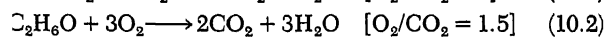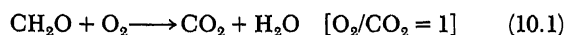
.s, oxidation of CH_4 rather than CH_2O yields only half as :h CO_2. All of these equations are valid for this site. How-r, because a large amount of the ΣCO_2 in excess is the ?rence between mixed water and final water, it is almost :ain that the mixing ratios for steps C and D, calculated on basis of Cl^- concentrations are in error.

'he mass-balance calculations suggest that between the land-and the first recovery well large amounts of organic matter lergo fermentation reactions and Fe- and Mn-containing les are mobilized. Fe and Mn are higher at the recovery than the landfill because (1) the landfill materials have been :hed of these metals since the material was emplaced, or the leachate comes in contact with more oxide coatings as noves downgradient. Most of the NH_4^+ exchange occurs ɪngradient of the landfill between wells 29 and 33, which he zone where the clay-confining layer becomes thicker. ? leachate that moves beyond the recovery well is subject oxidation as it mixes with native groundwater. Iron and nganese precipitate; concentrations of nitrate increase be-.se it is not subject to reduction. Farther downgradient, with exception of O_2 removal and ΣCO_2 generation, only small ıntities of constituents are involved in chemical reactions.

)NCLUSIONS

emical reactions and processes in contaminated water do : remain constant with time. Early diagenesis of landfill

materials produces high concentrations of ΣCO_2, NO_3^-, and SO_4^{2-}. During later stages, degradation of organic matter pro-ceeds until available sources of O_2 are consumed and the landfill becomes anaerobic. The main products formed are ΣCO_2, NH_4^+, H_2S, CH_4, Fe^{2+}, Mn^{2+}, and partially reduced organic matter. Sulfide may generate earlier than CH_4 or may be suppressed if methanogenic bacteria dominate. As the plume migrates through the aquifer, these processes change. Although CH_4 and NH_4^+ are not formed in the presence of O_2, they may remain in small concentrations after the water is partially ox-ygenated, whereas Fe^{2+} and Mn^{2+} will precipitate. Also, many organics, especially the chlorinated compounds, are insensitive to the presence of O_2.

Although zones of water with different chemical composi-tions develop by the oxidation and reduction of organic ma-terial, the boundaries and extent of these zones are controlled by competing rates of reaction and hydrologic transport. The fronts of these zones are transient because of the wide range in groundwater velocities and the dispersive character of the aquifer materials. If the flow is extremely slow in the aquifer relative to reaction rates, the plume will be attenuated more rapidly and the boundaries between zones may be noniden-tifiable. However, if the flow is fast relative to reaction rates, the zones will migrate farther downgradient and their bound-aries will be more distinct.

Plumes of leachate have migrated downgradient from the Army Creek landfill. The recovery-well system installed be-tween the landfill and major downgradient water-supply wells has successfully intercepted and removed most of the contam-inated water. At the Army Creek landfill, the attenuation of contaminants depends on the following: (1) operation of the recovery-well system that removes contaminated water and reverses the local flow, (2) dilution of leachate with native groundwater, (3) mixing of anaerobic leachate with oxygenated water that facilitates the decomposition of organic matter and precipitation of metals, and (4) interaction of contaminants with aquifer materials.

Measurements of the major chemical constituents in water immediately downgradient from the landfill show that most constituents have decreased in concentration since 1973, when the recovery system was put in operation. However, the leach-ate remains anaerobic, and large amounts of gases are being generated. With the exception of site S-1, concentrations of major constituents in landfill water have changed little with time. Site S-1 is in the newest part of the landfill and before 1981 the extremely high concentrations of constituents in water may be due to the mobilization of reactive materials and high rates of microbial activity. At site A-4, within the landfill, the pH, alkalinity, Cl^-, NH_4^+, and CH_4 measurements were sur-prisingly constant during the past 4 yr. Although the major inorganic constituents have changed little, the organic carbon content and the number of organic compounds identified in the leachate have greatly decreased. The refractory nature of many organic compounds and their tendency to remain coated on aquifer materials may cause a contamination problem for long periods of time. Organic contamination may be a threat even after the aquifer is returned to prelandfill conditions.

Concentrations of constituents in the leachate are deter-mined by the nature of the waste, by the amount of recharge

water that passes through the landfill, and by factors that control groundwater velocity. Hydrologic and chemical data during an 8-yr period indicate that the major changes beyond the anoxic-oxic boundary are controlled by physical processes rather than chemical reactions. Thus, the extent of leachate movement within the aquifer is determined by factors that influence groundwater velocity, which include the rates of pumping recovery and supply wells.

The recovery-well system has effectively retarded the movement of contaminants from Army Creek landfill to the Potomac aquifer. However, to achieve this retardation, pumping of water for supply has been curtailed and a significant amount of uncontaminated groundwater is wasted by pumping the recovery wells. Continued heavy pumping has lowered the head in the aquifer 15 m since the mid-1960s. As a result, saltwater intrusion is a threat to the eastern portion of the aquifer (Sundstrom, 1974). At this landfill, it is necessary to continue operation of the contaminant-recovery wells. If recovery wells are located close to the landfill, more remote wells can be abandoned and less uncontaminated water will be wasted. Using the aquifer alone to dilute and attenuate contaminants is an alternative, but it involves risks when the downgradient water must be potable. However, an evaluation of the aquifer material as an attenuating medium could be made in other areas where low concentrations of contaminants would not be objectionable in water downgradient.

ACKNOWLEDGMENTS

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Assessment of the Potential for Radionuclide Migration from a Nuclear Explosion Cavity

11

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INTRODUCTION

A field study of the distribution of radionuclides around an underground nuclear explosion cavity was initiated in 1974, about 9 yr after detonation of the nuclear test. This study is part of the Radionuclide Migration (RNM) Project, a broad investigation to determine the rates of migration underground in various media at the Nevada Test Site (NTS) and the potential for movement both on and off the NTS of radioactivity from underground nuclear explosions. It was also envisaged that the study might provide data applicable to the underground disposal of radioactive waste.

This ongoing project is sponsored by the Nevada Operations Office of the Department of Energy with the participation of the Los Alamos National Laboratory, the Lawrence Livermore National Laboratory, the U.S. Geological Survey, the Desert Research Institute, and appropriate support organizations.

The site of the 0.75-kiloton nuclear test Cambric, which was detonated beneath the water table in tuffaceous alluvium, was chosen for initial studies. It was anticipated that eventually tests in other geologic media would be examined.

Cambric was chosen for a number of reasons. The Cambric explosion cavity is within the NTS Area 5 water-supply aquifer, and there was particular interest in possible contamination of water supplies. It was predicted that sufficient time had elapsed so that the cavity and chimney had filled with groundwater to the preshot static water level, 73 m above the detonation point. If so, radionuclides might be present in the water and constitute a potential source for migration. The Cambric detonation point

is only 294 m below ground surface, and thus the re-entry drilling and sampling operations would be less difficult and expensive than for some of the more deeply buried tests. The site in Frenchman Flat is far enough from the areas of active nuclear testing so that damage or interruption of the re-entry and sampling operations from those activities would be unlikely. Sufficient tritium (^{3}H or T) was present to provide an easily measurable tracer for water from the cavity region. The postshot debris also contained plutonium, uranium, and fission products whose concentrations in the rubble and groundwater from the cavity and chimney regions could be measured and compared. A summary of the intensity of the radionuclide source term at the time of re-entry is given in Table 11.1. The small yield was expected to have had little effect on the local hydrology. Further, it was judged that the alluvium constituted a good medium for hydrologic studies because it was more permeable than tuff and did not have large fissures or cracks through which the water might selectively flow.

The Cambric cavity region was re-entered, and a well (RNM-1) was completed to a depth of 370 m. Samples were taken to determine the radionuclide distribution between the solid material and water at the time the experiment was started. Water was then pumped from a nearby satellite well (RNM-2S) to induce an artificial gradient sufficient to draw water from the Cambric cavity and provide an opportunity for the study of radionuclide migration under field conditions. A schematic diagram of the placement of RNM-1 and RNM-2S is shown in Figure 11.1. Details of the early stages of the RNM Cambric experiment are given in Hoffman et al. (1977) and Hoffman (1979).

TABLE 11.1 Cambric Source Term 10 Yr after Detonation

Nuclide	Half-Life (Yr)	Activity (Ci)
^{3}H	12.3	3.4×10^4
^{85}Kr	10.7	4.4
^{90}Sr	29	34
^{106}Ru	1.0	2.8
^{125}Sb	2.8	3.2
^{137}Cs	30	99
^{144}Ce	0.78	0.4
^{147}Pm	2.6	33
^{155}Eu	5.0	6.4

CAMBRIC RE-ENTRY

Three types of samples were recovered from the RNM-1 re-entry hole into the Cambric cavity: sidewall cores, pumped water, and water with contained gases. As drilling progressed, 67 sidewall core samples were taken from RNM-1 from 34 m below the surface to 50 m below the original detonation point (Figure 11.2). One core from each depth was placed immediately in a nitrogen-flushed, gastight, stainless-steel container for subsequent analyses of ^{85}Kr, HT, and HTO and for gamma-spectral analyses. Other core samples were sealed in watertight plastic bags for later gamma-spectral and radiochemical analyses to determine the concentrations of the various radionuclides present. The cores were also examined to determine the lithology of the medium at different depths. Solid samples and water removed from the sidewall cores from the lower cavity region were analyzed radiochemically for ^{90}Sr, ^{137}Cs, and ^{239}Pu, and effective distribution coefficients (ratio of the concentration in or on the solid to the concentration in the aqueous
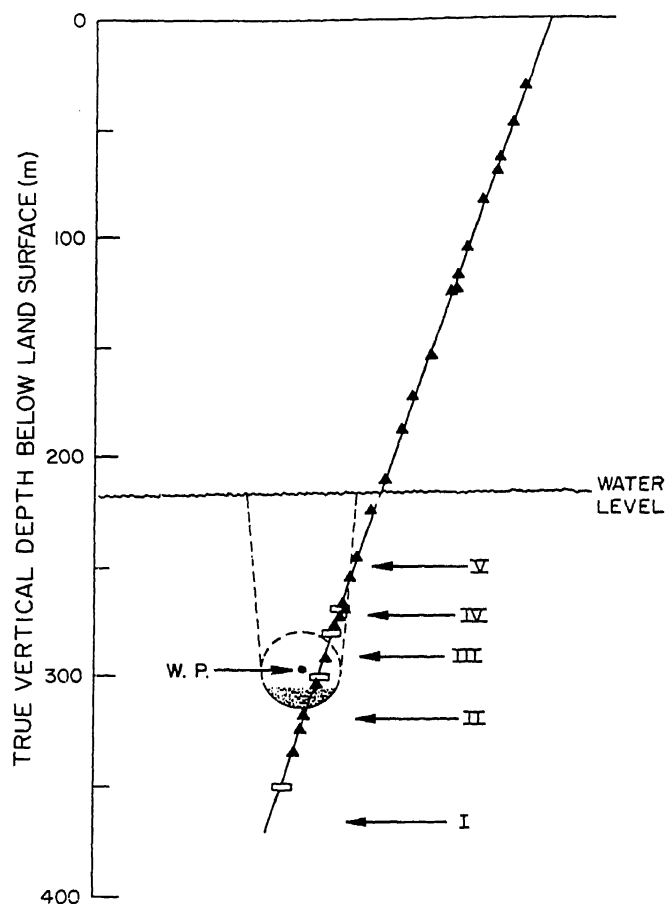
FIGURE 11.2 Locations of sidewall core samples taken from RNM-1 (triangles). Roman numerals indicate locations of isolated water sampling zones. The detonation point is indicated by W.P.

phase) were determined (Table 11.2). These effective distribution coefficients are a measure of both retention in the fused material and sorption. The radionuclides were found to be almost entirely incorporated in or on the solid material.

After sidewall core sampling had been completed and the hole had been cleaned, casing was installed with appropriately placed, inflatable, external packers. The packers were used to minimize external water movement in the annular space between the casing and the wall. Beginning at the bottom, the water in five zones was sampled successively by isolating the

FIGURE 11.1 Schematic of RNM-1 and RNM-2S.

TABLE 11.2 Effective Distribution Coefficients in the Lower Cavity Region

Nuclide	Distribution Coefficient (mL/g)
^{90}Sr	10^4
^{137}Cs	$>10^4$
^{239}Pu	10^6

zones with internal packers and perforating the casing (Figure 11.3). Gastight water samples were taken at depth, and additional water samples were removed to the surface by a submersible pump. Representative activity levels of the radionuclides detected in water from each zone are given in Table 11.3. Ten years after the test most of the radioactivity and the highest concentrations of all radionuclides were still found in the region of the original explosion cavity. No activity was found 50 m below the cavity. Measurements of HT and HTO removed from the cores and gastight water samples showed that more than 99.9 percent of the tritium was present as HTO. Although some ^{85}Kr and tritium were found in the collapsed zone above

the explosion region, they were concentrated in the cavity region. The measured ^{85}Kr-to-tritium ratios for water from the explosion cavity zone were consistent with the relative amounts resulting from the Cambric test; the ^{85}Kr seemed to be dissolved in the water. No ^{85}Kr was observed in water or solid material from cores taken above the water table. Water from the region of highest radioactivity at the bottom of the cavity contained only tritium and ^{90}Sr at levels higher than the recommended concentration guides (CG) for water in uncontrolled areas (Standards for Radiation Protection, 1977; National Interim Primary Drinking Water Regulations, 1978).

By comparing the measured ratio of each nuclide detected

FIGURE 11.3 Construction details of RNM-1 in and near the lower part of the Cambric chimney. Roman numerals indicate isolated water sampling zones. The original emplacement hole was designated U-5e.

TABLE 11.3 Representative Activity Levels in Cambric Water Samples 10 Yr after Detonation

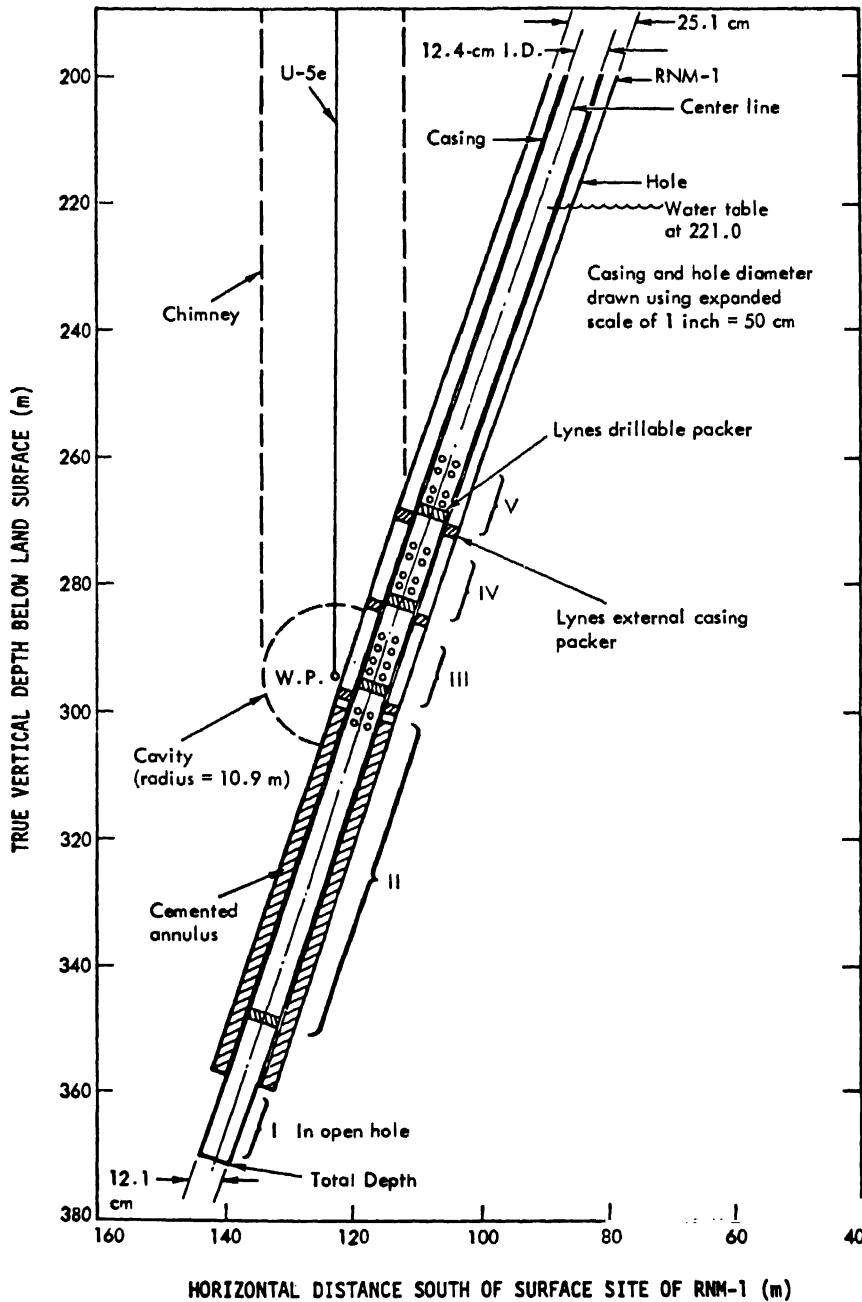| Zone	Tritium Activity Level (μCi/mL)	Activity Level (dpm/mL)					
		^{85}Kr	^{90}Sr	^{106}Ru	^{125}Sb	^{137}Cs	^{239}Pu
Below cavity	bg[a]	bg	bg	bg	bg	bg	bg
Lower cavity	6.1	800	8	11	5	1.6	≤0.003
Upper cavity	3.8	1200	5	4	2	1.4	≤0.003
Chimney	0.084	70	5	nd[b]	nd	0.8	nd
Adjacent to chimney	0.028	20	0.2	nd	nd	0.2	nd
CG[c]	2×10^{-5}	—	0.018	22.2	222	44.4	11.1

[a]bg, no activity detectable above background levels.

[b]nd, not detected.

[c]CG is the recommended (*Standards for Radiation Protection*, 1977; National Interim Drinking Water Regulations, 1978) concentration guide applicable to water in uncontrolled areas. Values for tritium and ^{90}Sr in public drinking water standards established in National Interim Drinking Water Regulations (1978).

in the water to the tritium in the water with the calculated ratio for the Cambric source term, an effective overall retention factor, E_d, for each nuclide (ratio of the total activity in or on the solid to the total activity in the aqueous phase) was estimated. (This calculation assumes that all the radionuclides had been retained below the water table and that the fraction of a nuclide not in the water was in the solid.)

$$E_d = \frac{(A_X/A_T)_{\text{Cambric}} - (A_X/A_T)_{\text{water}}}{(A_X/A_T)_{\text{water}}} = \frac{(A_{X\ \text{Cambric}})(A_{T\ \text{water}})}{(A_{X\ \text{water}})(A_{T\ \text{Cambric}})} - 1.$$

Substituting $\dfrac{A_{T\ \text{water}}}{A_{T\ \text{Cambric}}} \geq 0.999 \approx 1$,

$$E_d = \frac{A_{X\ \text{Cambric}}}{A_{X\ \text{water}}} - 1.$$

Then

$$E_d = \frac{A_{X\ \text{solid}}}{A_{X\ \text{water}}} \approx K_d \frac{\Sigma g_{\text{solid}}}{\Sigma cc_{\text{water}}}$$

or

$$K_d \approx E_d \frac{\text{wt. \% water}}{100 - \text{wt. \% water}},$$

where K_d is the distribution coefficient.

The nuclides ^{90}Sr, ^{106}Ru, ^{125}Sb, ^{137}Cs, ^{147}Pm, and ^{239}Pu were all found to have high retention factors, indicating that they are either retained in the fused debris, highly sorbed on the solid material, or both (Table 11.4).

SATELLITE WELL

The satellite well RNM-2S was located 91 m from the Cambric explosion cavity. Pumping was begun in October 1975 at a rate of about 1 m³/min; in October 1977 the rate was increased to about 2.3 m³/min. Significant amounts of tritiated water, signaling arrival of water from the Cambric cavity region, were finally detected after a total of about 1.44 million m³ of water had been pumped from the satellite well. After almost 6 yr of pumping, the tritium concentration in the pumped water appears to have reached a maximum, as shown in Figure 11.4. Discontinuities in the plot correspond to periods during which the pump was not operating.

Since the observation of tritium in water from the satellite well, samples with contained gases have been taken by pumping from RNM-2S and from RNM-1. Results for such samples from the satellite well indicate the presence of ^{85}Kr (Figure 11.5), a gas that apparently was retained in the water during transit. The ^{85}Kr/tritium atom ratios are shown in Figure 11.6. It should be noted that these are relatively constant at a value of approximately 0.4×10^{-4}, considerably lower than that of 1.22×10^{-4} calculated for Cambric. So far the reason for this is not known; however, this result may very well be related to events occurring at RNM-1. The pump and packers in RNM-1 were left in a configuration such that pumping removes water from Zones IV and V (Figure 11.3), which are just above the cavity region; most of the water production is believed to be from Zone IV. Data for water pumped from RNM-1 are pre-

TABLE 11.4 Retention Factors from Cambric Water Samples

Zone	^{90}Sr	^{106}Ru	^{125}Sb	^{137}Cs	^{147}Pm	^{239}Pu
Below cavity	bg[a]	bg	bg	bg	bg	bg
Lower cavity	2.1×10^3	1.0×10^2	2.9×10^2	2.5×10^4	$>10^6$	$>3.2 \times 10^7$
Upper cavity	1.6×10^3	1.9×10^2	3.6×10^2	1.8×10^4	nd	$>1.9 \times 10^7$
Chimney	3.9×10^1	nd[b]	nd	6.6×10^2	nd	nd
Adjacent to chimney	3.1×10^2	nd	nd	1.1×10^3	nd	nd

[a]bg, no activity detectable above background levels.

[b]nd, not detected.
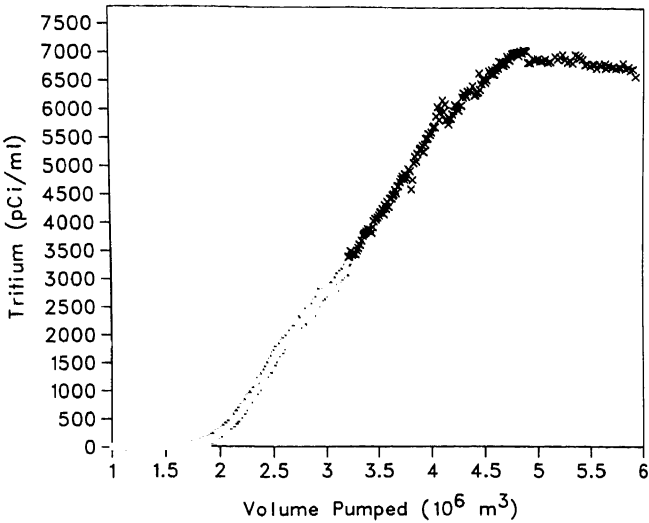
FIGURE 11.4   Tritium concentration in water from RNM-2S, corrected to Cambric zero time.

FIGURE 11.6 ^{85}Kr/T atom ratios for water from RNM-2S. The calculated value for Cambric is 1.22×10^{-4}.

FIGURE 11.5 ^{85}Kr concentration in water from RNM-2S, corrected to Cambric zero time.

sented in Table 11.5. The concentrations of tritium and ^{85}Kr in water from RNM-1 have decreased by more than a factor of 100, presumably as a result of pumping at the satellite well; however, the ^{85}Kr concentration is apparently decreasing more slowly than the tritium concentration. The ^{85}Kr/tritium ratios obtained for samples collected from RNM-1 since pumping began at the satellite well are consistently greater than the calculated ratio.

More than a dozen 55-gallon (0.21-m^3) water samples, taken at intervals from RNM-2S since the first observation of tritium, have been reduced to solid residues by evaporation, and the gamma-ray spectra of these residues have been measured. With the possible exception of a very small amount of ^{106}Ru — concentration <1 percent of that produced in Cambric (Coles and Ramspott, 1982) — no gamma-emitting nuclides have been identified in these samples. Radiochemical analyses of other water samples for the beta-emitting nuclide ^{90}Sr have also given negative results.

TABLE 11.5   Tritium and ^{85}Kr Activity Levels[a] in RNM-1 Gastight Water Samples

Entry	Date	Volume of Water from RNM-2S (m^3)[b]	T (nCi/mL)	^{85}Kr (dpm/mL)	^{85}Kr/T (atom ratio)[c]
Original-Zone IV	8/8/75	0	150	70	1.8×10^{-4}
Original-Zone V	8/14/75	0	38	13	1.3×10^{-4}
Re-entry I[d]	10/4/77	1.17×10^6	3.2	75	9.4×10^{-3}
Re-entry II[d]	11/30/77	1.34×10^6	2.0	6	1.3×10^{-3}
Re-entry III[d]	9/4/79	3.50×10^6	0.26	0.57	8.8×10^{-4}

[a]All activity levels corrected to Cambric zero time.
[b]Volume of water removed from RNM-2S by indicated date.
[c]The calculated ^{85}Kr/T atom ratio for Cambric is 1.22×10^{-4}.
[d]The packer between Zones IV and V was drilled out before pumping was started at RNM-2S. Water pumped for "re-entry" samples can enter from perforations in both Zones IV and V, but most of the water is believed to be from Zone IV.

After removal of more than 5.6 million m³ (over 1.5 billion gallons) of water from the satellite well, only tritium, which is present as HTO and chemically the same as the water, and ^{85}Kr, which seems to be dissolved in the water, have been positively identified in water from RNM-2S.

The arrival of tritium at the satellite well was compared (R. S. Rundberg, Los Alamos National Laboratory, personal communication, 1981) with the calculations of Sauty (1980) for an instantaneous tracer injection in a radial, converging flow field, similar to the Cambric experiment. The shape of the elution curve depends on the Peclet number, which is inversely proportional to the dispersivity. The smaller the Peclet number the greater the dispersion, i.e., the broader and more skewed the elution peak. In order to compare the experimental data with the calculation, dimensionless time, T_R, and dimensionless concentration, C_R, must be used. The dimensionless time is time T divided by the time when the maximum of the elution peak occurs; the dimensionless concentration is the concentration at T divided by the maximum concentration.

Since the maximum in the tritium concentration in water from RNM-2S is not yet well defined, a calculation was made based on the amount of tritium pumped from RNM-2S by July 6, 1981, specifically 24 percent of that produced in Cambric. Values for T_R and C_R were determined for the same date (5.60 × 10⁶ m³ of water pumped) by locating the point on calculated curves of Sauty (1980) corresponding to elution of 24 percent of the total tracer. The available calculated curves for several Peclet numbers were thus compared with the normalized experimental data (Figure 11.7). It appears that a calculated curve for a Peclet number between 3 and 10 (dispersivity between 30 and 10 m) would best fit the experimental data. This result can be compared with the data presented by Borg *et al.* (1976), who reported longitudinal dispersivity values that were estimated by calibrating mathematical models for transport against observed transport. Values ranged from 11.6 to 91 m for a wide variety of lithologies. The dispersivity for a sand and gravel deposit, the lithology probably most closely resembling the

tuffaceous alluvium of the current experiment, was found to be 21.3 m.

LABORATORY EXPERIMENTS

Laboratory experiments have primarily involved measurement of the partition of various radionuclides of interest between groundwaters and crushed rock samples of various geologic media ("batch" studies). Some experiments involving the leach rates for the removal of various radionuclides from nuclear test debris have also been performed. In general, the rates for removal of a radionuclide from such debris were found by Wolfsberg (1978) to be quite low (Table 11.6).

Results for the batch measurement of the sorption of a number of radionuclides on tuffaceous alluvium and bentonite are given in Table 11.7. The sorption properties of tuffaceous alluvium are comparable with those of bentonite, which is being considered for use as an engineered barrier because of its excellent sorptive properties. Sorption-desorption equilibria are approached slowly, and results obtained for sorption measurements, where the tracer is initially present in the aqueous phase, and for desorption measurements, where the tracer is initially present in the solid phase, frequently differ. We therefore emphasize that "distribution coefficients" calculated from such data may represent nonequilibrium conditions. In addition, it should be noted that such values for the laboratory experiments refer only to sorption phenomena and do not include the effects of retention in fused debris as do the results given in Table 11.2. The "irreversible" sorption or much slower desorption may be due to speciation changes, diffusion into minerals, crystallization reactions on solids, or nonionic sorption of colloids or precipitates. These possibilities require further investigation.

A comparison of the results from laboratory sorption experiments (Table 11.7) and calculated retention factors from Cambric water samples (Table 11.4) indicates that most of the radioactivity from the explosion is incorporated in the fused debris rather than sorbed. In the upper cavity and chimney regions, where sorption is presumably the dominant process, the laboratory results and retention factors from field data are comparable.

The sorptive properties of tuff have been extensively studied (Wolfsberg *et al.*, 1979, 1981; Vine *et al.*, 1980), and it has been demonstrated that there are minerals in the varieties of tuff at the Nevada Test Site that exhibit excellent sorptive properties for cations. Such tuffs should provide a natural barrier against radionuclide migration to the biosphere.

Most nuclides were found to sorb well on the geologic media studied; however, sorption of anionic species such as those of iodine, technetium, and uranium, which is frequently complexed by carbonate in the groundwater, is normally quite low for all geologic media (see Table 11.7). The chemistry of the actinides and lanthanides in groundwaters is complex and poorly understood. Research is necessary to achieve proper understanding of actinide and lanthanide chemistry in near-neutral solutions for adequate prediction of transport behavior in natural systems.
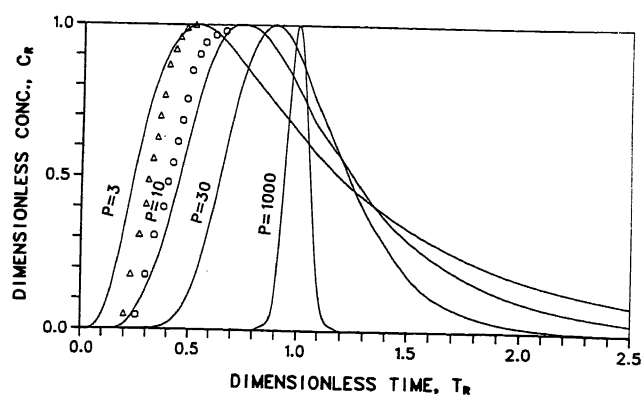

FIGURE 11.7 Calculated elution of tracer for instantaneous tracer injection in a radial converging flow field for Peclet numbers 3, 10, 30, and 1000 (from Sauty, 1980). Normalized data for tritium observed in RNM-2S water are shown by triangles for $P = 3$ and by circles for $P = 10$.

TABLE 11.6 Leaching Data for High-Graded Refractory Debris

Nuclide	Test Location: Shaking Time (Days):	Fraction Leached Ground Material U3km 23.6	U3ki 23.6	Chunks U7ap 35.3	U7ap 35.3ᵃ
^{54}Mn				2.9×10^{-4}	9.0×10^{-5}
^{85}Co				4.4×10^{-4}	9.6×10^{-5}
^{88}Y		$<8 \times 10^{-5}$	$<6 \times 10^{-5}$	$<8 \times 10^{-4}$	$<2 \times 10^{-4}$
^{95}Zr		$<8 \times 10^{-6}$	$<2 \times 10^{-6}$	$<4 \times 10^{-5}$	$<5 \times 10^{-5}$
^{106}Ru		9.6×10^{-5}	3.1×10^{-5}	5.1×10^{-5}	1.3×10^{-5}
^{124}Sb		5.0×10^{-3}	2.6×10^{-3}	2.5×10^{-4}	4.4×10^{-4}
^{126}Sb		5.6×10^{-3}	2.9×10^{-3}		
^{129}Te^m		2.7×10^{-3}	1.8×10^{-3}	9.6×10^{-3}	1.5×10^{-3}
^{131}I		2.0×10^{-2}	1.4×10^{-2}	8.8×10^{-3}	7.8×10^{-3}
^{137}Cs		$<2 \times 10^{-3}$	$<2 \times 10^{-3}$		
^{140}Ba		6.5×10^{-5}	5.1×10^{-5}	2.2×10^{-4}	9.6×10^{-5}
^{141}Ce		$<2 \times 10^{-6}$	$<1 \times 10^{-6}$	$<4 \times 10^{-6}$	$<3 \times 10^{-5}$
^{181}W		1.1×10^{-2}	3.8×10^{-3}	1.2×10^{-3}	3.5×10^{-4}
^{188}W		7.7×10^{-3}	4.5×10^{-3}		
^{182}Ta		$\leq 3 \times 10^{-4}$	$\leq 2 \times 10^{-4}$		
^{237}U		2.5×10^{-3}	1.2×10^{-3}	6.1×10^{-4}	2.6×10^{-4}
^{239,240}Pu		$<6 \times 10^{-6}$	$<5 \times 10^{-6}$		

ᵃSolution and container were purged with Ar before leaching.

The transport of tritium, which is assumed to have a distribution coefficient of zero, took over 2 yr to reach RNM-2S. We estimate that more than 13 yr would be required at current pumping rates for a hypothetical radionuclide with a distribution coefficient of only 1 mL/g to travel the 91 m between the explosion zone and the satellite well. The laboratory experiments indicate that most elements have K_d values much greater than this (see Table 11.7) and would not be expected

in water from the satellite well for many years. For example, strontium has a K_d of approximately 200 mL/g and would not reach RNM-2S for 1500 yr. Nonequilibrium effects or the presence of colloidal or other nonsorbing species might allow some nuclides to move more rapidly than expected; therefore, monitoring for radionuclides in water pumped from RNM-2S is continuing.

TABLE 11.7 Distribution Coefficients for Alluvium and Bentoniteᵃ

Element	Distribution Coefficient (mL/g) Alluvium Sorption	Desorption	Bentonite Sorption	Desorption
U(VI)	6	60	200	170
Sb	6	80	7	50
Sb^b	30	220		
Mo^b	20			
I^b	0.15	4.6		
Sr	220	180	1700	2500
Ru^b	10	300		
Nb	1900	3500	1000	2200
Ba	3800	4000	4000	6000
Cs	8000	8000	1800	2200
Co	9000	21,000	1300	7000
Ce	>20,000	>2000	>500	>2000
Eu	>5000	>2000	>1400	>6000

ᵃData from Wolfsberg (1978) and Wolfsberg and Wanek (1982).
^{b}Trace water produced by leaching test debris.

SUMMARY AND CONCLUSIONS

The source term for radionuclides in the region of the Cambric nuclear explosion has been determined. Drillback cores were obtained and analyzed, and water was pumped from several vertical zones and analyzed. Most of the radioactivity produced in the test was found to be retained in the fused debris with only low concentrations in the water that had been in contact with the debris for nearly 10 yr. Most of the radioactivity and the highest specific activities of all radionuclides were found to be in the region of the original explosion cavity. No activity was found 50 m below the cavity. Water from the region of highest radioactivity at the bottom of the cavity contained only tritium and ^{90}Sr at levels higher than the recommended concentration guides for water in uncontrolled areas.

During nearly 6 yr (over 1.5 billion gallons of water) of pumping from a satellite well located 91 m from the Cambric cavity, only tritium, which is present as HTO and chemically the same as the water, and ^{85}Kr, which seems to be dissolved in the water, have been positively identified in water removed from this well, although there is some evidence for the possible migration of minute amounts of ^{106}Ru. These results are consistent with laboratory studies, which indicate that, in general, radionuclide sorption is sufficiently high to preclude the migration of such nuclides from the original cavity to the satellite well in the near future. Pumping and radioassay of water from the satellite well will be continued to investigate the possible arrival of nonsorbing species.

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Groundwater Restoration with In Situ Uranium Leach Mining

12

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INTRODUCTION

In situ leach mining of uranium (U) has developed into a major mining technology, which compares favorably with traditional open pit mining and underground mining for recovery of U ore. Since 1975, when the first commercial mine was licensed in the United States, the percentage of U produced in the United States by in situ mining has grown steadily from 0.6 percent to 10 percent in 1980. Part of the reason for this growth is that in situ mining offers less initial capital investment, shorter start-up times, greater safety, and less labor than conventional mining methods. There is little disturbance of the surface terrain or surface waters, no mill-tailings piles, and no large open pits. Also, many of the hazards of working in a U-processing plant are reduced.

In situ leach mining also has environmental disadvantages. During mining, large amounts of groundwater are circulated and there is some withdrawal from an area where aquifers constitute a major portion of the water supply for other purposes. When an ammonia-based leach system is used, the ammonium ion is introduced into an area where cation exchange on clays (and some production of nitrate) may occur. Also, injection of an oxidant with the leach solution causes valence and phase changes of indigenous elements such as As, Cu, Fe, Mo, Se, S, and V as well as U. Thus, other species along with uranium may be solubilized. Furthermore, the surrounding groundwater can become contaminated by escape of the leach solution from the mining zone.

Following mining, the water in the mined zone is left with an ionic strength that exceeds the natural baseline level for some constituents. In particular, much attention has been di-rected toward the high (relative to baseline) ammonium concentration, following leaching with an ammonium-based system, and toward the fate of heavy metals solubilized during the mining process. A question of major interest concerns restoration of the sites, since many of the mining intervals or horizons coincide with fresh groundwater. Restoration is necessary to reduce the amounts of undesired chemical constituents left in solution after mining operations have ceased and thus to return the groundwater to a quality consistent with pre-mining use and potential use.

The questions and problems faced by the in situ mining industry, and by those who regulate it, are representative of those faced by any developing industry that has the potential for causing adverse environmental changes on a valuable resource. This chapter presents an overview of the in situ mining technology, including U deposition, mining techniques, and groundwater restoration alternatives. The latter part of the chapter covers the situation in South Texas. Economics and development of the industry, groundwater resources, regulation, and restoration activities are also reviewed.

URANIUM DEPOSITION IN SANDSTONE

The principal regions in the United States with potential U recoverable by in situ leach mining are the Wyoming Basins, the Colorado Plateau, and the Gulf Coastal Plain of Texas. The southern Black Hills and northeastern Colorado, within the Great Plains region, also contain sedimentary U deposits that may be amenable to in situ leach mining. The formation of a U deposit requires five factors: a source of U, a transporting

media, a host rock, a trapping mechanism, and a preservation mechanism. The U in sandstone-type deposits is thought to have been derived from either granite or volcanic material that was deposited with, or later than, the sandstone. Oxygenated groundwater percolating through these units oxidizes and mobilizes the U and other minerals. The U-enriched groundwater moves downdip in the sandstone until it reaches an interface between oxidizing and reducing groundwaters. At this interface the U and other elements, including As, Se, V, Cu, and Mo, precipitate out of solution. Such deposits are called "roll-front" deposits. Typically they follow the general trend of the drainage channels. Individual ore bodies in sandstone lenses tend to be long and narrow but rarely exceed 100 m in length. These deposits are usually bounded above and below by impermeable mudstones or shales and are interspersed with clay stringers. Geologically and mineralogically, the deposits are similar. The ore is unoxidized, with the principal ore minerals being uraninite [$(U_{1-x}^{+4}, U_x^{+6})O_{2+x}$; ideally, UO_2] and coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$]. Because of the mode of transport and deposition, many U deposits coincide with fresh groundwater aquifers (Ford, Bacon, and Davis Utah, Inc., 1979).

MINING TECHNOLOGY

When exploration indicates the existence of an ore body, a sampling, testing, and monitoring program is established to determine the extent and quantity of ore, baseline water quality, and optimal well pattern design. Observation wells are located in front of, in, and behind the ore body in the ore-bearing aquifer and in any aquifers directly above and below the ore horizon. Monitor wells are also drilled at the sides of the ore zone to encircle the production site and within the containment area to monitor excursions (Geraghty & Miller, Inc., 1978). After the necessary permits are obtained, production can begin.

In situ leach mining is that method by which the ore mineral, in the original geologic setting, is preferentially leached from the host rock by the use of specific leach solutions and the mineral recovered. The leach solution, or lixiviant, is introduced into the formation through injection wells. Once in the formation the leach solution oxidizes, complexes, and mobilizes the ore. The enriched, or pregnant, solution is then removed from the formation through production wells. At the surface the U in the pregnant solution is recovered by ion-exchange techniques. The residual U-barren solution from the ion-exchange operation is regenerated with suitable leaching chemicals and recirculated to the well field for reuse. To minimize the likelihood of migration of the leach solution from the production zone, the system is usually operated with more solution being withdrawn than injected. This excess withdrawal is referred to as the "bleed." It is disposed of through solar evaporation and deep-well injection.

Once a suitable loading has been achieved on the exchange resin, the ion-exchange column is removed from the production stream and the resin is cycled to the elution step. During elution, the resin is contacted with a chemical solution that

strips the U from the resin; the resulting product solution is termed the eluate, and eluted resin is recycled to the loading operation. The U is recovered from the eluate by precipitation. Following thickening and filtration, the final product is primarily ammonium diuranate, a yellow-colored precipitate or slurry termed *yellow cake*. The filter cake can then be dried and packaged for shipment (Larson, 1978).

During development of the in situ mining industry, leaching experiments were carried out with two major types of leaching systems. Acid-leaching systems use the sulfate of dilute sulfuric acid as the chelating agent with the U mobilized as the uranyl sulfate complex, $UO_2(SO_4)_3^{-4}$. In the presence of significant $CaCO_3$, large amounts of acid are required and there are problems with precipitation of $CaSO_4$. Generally, acid-leaching systems have not found significant in situ use. Alkaline, or carbonate, leaching systems have used carbonates and bicarbonates of ammonium and sodium to complex the U into the uranyl tricarbonate form, $UO_2(CO_3)_3^{-4}$. Many of the early commercial operations used an ammonium carbonate-bicarbonate leach with hydrogen peroxide as the oxidizing agent. The leach solution is made by adding from 0.5 to 2.0 g/L H_2O_2 and from 0.5 to 10.0 g/L of the NH_4-HCO_3-CO_3 species to the groundwater. Typical values for H_2O_2 are less than 1.0 g/L (Kidwell and Humenick, 1981), while those for the NH_4 species vary from 1 to 3 g/L (D. Tweeton, U.S. Bureau of Mines, personal communication, 1982). Oxidation results from the decomposition of H_2O_2 to water and oxygen. Uranium is recovered as $(NH_4)_4UO_2(CO_3)_3$. In the presence of certain clays, ammonium is exchanged for other cations. This exchanged ammonium is difficult to remove during restoration. To avoid the problem of ammonium restoration the industry has moved to the use of a sodium carbonate-bicarbonate leach with oxygen as the oxidizing agent. Although cation exchange does not present a restoration problem with this leach, the presence of sodium can cause dispersion of certain clays and resulting loss of permeability. It appears that this is less of a problem at a moderate rather than a high pH; however, research on leaching is continuing. Recently there has been interest in a potassium carbonate-bicarbonate leaching system. This system may avoid both the problems of difficult restoration faced by the ammonium system and potential loss of permeability faced by the sodium system. The primary obstacle standing in the way of the potassium carbonate-bicarbonate lixiviant is its expense. In late 1980, 1 kg-mole of potassium bicarbonate cost $31, whereas 1 kg-mole of ammonium bicarbonate cost $8 and 1 kg-mole of sodium bicarbonate cost $7 to $8 (U.S. Bureau of Mines, 1981). Researchers in petroleum engineering at the University of Texas at Austin have developed the use of a KCl preflush. This preflush satisfies the cation exchange sites with potassium before leaching and reduces the consumption of potassium carbonate-bicarbonate during leaching. Because the cost of KCl is relatively low (about $5/kg-mole), the cost of using potassium carbonate-bicarbonate is reduced. An additional benefit of the KCl preflush is better maintenance of permeability. Also, in laboratory experiments, the chloride preflush did not reduce U recovery. If the potassium lixiviant is used with a KCl preflush, it may be cost competitive with either the ammonium or sodium leaches (U.S. Bureau of Mines, 1981).

GROUNDWATER RESTORATION
ALTERNATIVES AFTER LEACH MINING

A strategy for restoration is necessary to reduce the amounts of undesired materials left in solution after operations have ceased and thus return the groundwater to a quality consistent with pre-mining use and potential use. In situ U mining affects groundwater quality directly by the introduction of compounds with the leaching solution and indirectly by the release of materials such as heavy metals from dissolution of minerals present in the rocks. Ammonium is an example of a compound that may be introduced into an aquifer during the mining process. Although ammonium systems are no longer in general use by the U-mining industry, they were the primary leaching system used during the initial period of development. Ammonium may be innocuous in the subsurface, but since it may oxidize to nitrates, a mobile species for which an EPA drinking water standard of 10 mg/L of nitrogen has been established, much attention has been focused on the question of ammonium restoration. This topic is addressed later in this chapter. The question of the release of heavy metals and other materials during mining is still of major concern. Kidwell and Humenick (1981) investigated trace groundwater contaminants released during mining (in South Texas) and found that U was the major trace element to appear in significant quantity during groundwater sweeping (discussed below) of a leached area. They also found that leaching operations can rapidly solubilize Mo, but that its concentration declined to EPA limits within a few pore volumes of groundwater sweep if it was not recycled in the leaching solution. Arsenic was found to be released after a period of time, though in minor amounts, and V and Se concentrations were not found to be significant. Of major interest is their conclusion that groundwater sweeping may restore the production area, and the extent of the sweep depends on the U content and time needed to leach the ore but not on the strength of the oxidant used.

Groundwater restoration entails a range of techniques from in situ processes within the aquifer to surface-separation processes that treat the water at the surface for later reinjection to the former production zone or disposal by other means and finally to ultimate disposal methods that dispose of the water that is not feasible to treat. In fact, most strategies involve a mix of in situ techniques, surface-separation processes, and ultimate disposal methods to achieve restoration. A more detailed discussion of restoration methods is given in the report by Ford, Bacon, and Davis Utah, Inc. (1979) and by Charbeneau *et al.* (1981).

During the initial phase of restoration, water containing the highest concentrations of contaminants is produced from the mining zone. These first few pore volumes are usually disposed of by partial evaporation and subsequent deep-well injection. Following this initial phase of restoration, in situ methods may be applied. The simplest strategy is to suspend restoration activity in the aquifer after disposal of the first few pore volumes from the production zone. In this way the physicochemical actions at work within the aquifer, including reduction, neutralization, precipitation, and adsorption, may restore the groundwater naturally. Natural processes are important in all restoration schemes because they provide the mechanism by which the aquifer is stabilized after the groundwater quality has been preliminarily restored and because they may reduce the need for extensive surface treatment. However, restoration based on natural processes has never been proposed by an operator nor approved by any state or federal agency. The mechanisms of natural restoration are complex, and the important physicochemical properties are highly variable. This makes it difficult to provide evidence and assurance of improvement in groundwater quality by natural mechanisms. Despite these uncertainties, natural restoration may yet prove to be adequate to protect the environment. A number of methods have been suggested to enhance in situ restoration. These include biological nitrification, bacterial precipitation, and chemical precipitation.

Associated with the in situ and surface-separation processes of restoration are the methods for removal of water from the aquifer—groundwater sweeping and groundwater recirculation. In a groundwater sweep, injection operations are curtailed and a number of wells are used as production wells, which draw water from the contaminated part of the aquifer (production zone) and draw cleaner water from the nonaffected part of the aquifer. This method may be conducted with surface separation and reinjection of the treated water into the aquifer at a point away from the production zone, or it may be conducted without recharge in order to draw exclusively from the undisturbed waters outside the production zone. Because there is no recharge, the fluid migrates uniformly to the production wells. After such a sweep, the water may be disposed of by deep-well disposal, by solar evaporation ponds, or by irrigation or runoff to surface flows.

Restoration by groundwater recirculation is achieved through the continued pumping through the same production and injection wells used in the mining operations, except that the direction of induced flow may change and the groundwater is reinjected without being reconstituted with the leaching solution (lixiviant). Recirculation may be conducted either as forward recirculation, in which the same wells are used as in the mining process for production and injection, or as reverse recirculation, wherein the mining injection wells are converted to production wells and the mining production wells are converted to injection wells. If a continued five-spot well pattern is used in the mining process, the major distinction between forward and reverse recirculation concerns the behavior of the boundary wells. With forward recirculation the lixiviant is pushed further away from the injection wells along the streamlines of the flow field. If the system is operated with a bleed, then the lixiviant will eventually be pushed into a production well and recovered. In the case of reverse recirculation the lixiviant is pulled back along the same streamlines to the former injection wells and recovered. There are trade-offs between forward and reverse recirculation, and a system may be designed so that only some of the mining wells operate and the system is a mix between forward and reverse recirculation. In any case, this continued circulation enhances the natural physicochemical processes referred to earlier. Additionally, production water could be processed or treated at the surface to reduce chemical concentrations to background levels and then reinjected into

the aquifer to leach additional contaminants. Also, the processed solution could be constituted with compounds that enhance restoration before reinjection.

Surface-separation processes consist of pumping contaminated water from the underground production area and treating the water in a suitable treatment plant at the surface. The treated water may be used as recharge to the aquifer or otherwise disposed of depending on the quality characteristics of the final effluent from the treatment plant. The residuals from the treatment process must be disposed of properly to avoid undesirable pollution of surface waters or of the land. Because of the characteristics of the production water from in situ mining, physicochemical processes are applicable for the treatment of the contaminated water before its final disposal. These processes include reverse osmosis, electrodialysis, distillation, chemical precipitation, adsorption, ion exchange, foam fractionation, and freeze separation. A 1978 ranking of separation methods to produce a water satisfactory for recharge is presented by Ford, Bacon, and Davis Utah, Inc. (1979). Reverse osmosis and recharge with either deep-well disposal or solar evaporation of the treatment waste appears to be the most economically effective technique. The system costs ($/1000 gallons) for recharge/reverse osmosis/deep-well disposal and recharge/reverse osmosis/solar evaporation and pond disposal are $1.78 and $2.19, respectively. More recent information indicates that electrodialysis is now competitive with reverse osmosis (Garling, 1981). The separation processes have as their objectives the production of a water suitable for recharge to the aquifer. If recharge is not required to meet quantity demands from the aquifer, sweeping and deep-well disposal or sweeping followed by solar evaporation of the sweep water in properly designed and constructed ponds may be the preferred restoration scheme.

A major part of any restoration scheme is the choice of method or methods for ultimate disposal of the wastes. Two methods are available: (1) deep-well injection and (2) evaporation in ponds followed by solid-waste disposal of the sludge and residue. During restoration, at least the first few pore volumes containing the most heavily contaminated water are disposed of either through deep wells or evaporation in ponds. This is necessary because in situ methods are inadequate and surface-separation methods are infeasible to effect restoration of such water. A major advantage of deep-well disposal over surface-disposal methods is that the objectionable waste solution is completely removed from the environmentally sensitive biosphere. Deep-well disposal systems are limited to solutions with low-suspended solids and turbidity and solutions that will not plug the injection zone by the precipitation of solids in reactions between the waste and the solutions and solid matrix of the host aquifer. The solar-evaporation pond process reduces the volume of wastewater but generates a sludge residue that must be impounded. Solar-evaporation ponds are effective for the disposal of most pollutants from groundwater restoration. Solid-waste-disposal schemes are required for the solid wastes generated. The solid-waste-disposal system is required to collect, store, treat, handle, transport, place, and secure the objectionable materials.

IN SITU URANIUM MINING IN SOUTH TEXAS

The previous sections have suggested that U is deposited locally along with additional potential contaminants, that the in situ mining process solubilizes the U and other materials, and that a number of restoration options are available to return the groundwater to a state compatible with pre-mining use and potential use. It is important to realize that the technology is new and that large-scale restoration, while in progress, has not been fully achieved to date. Estimates as to the ease or difficulty of restoration are based on laboratory studies and small-scale prototype operations. At present, it appears that restoration is possible but that the amount of water and energy use depends on the restoration method(s) applied and on site-specific factors.

In the following sections the in situ U-mining technology as developed and practiced in South Texas is discussed. Along with industry development and the present status of restoration activities, both the groundwater resources and regulation are reviewed.

Development and Economics of In Situ Mining in South Texas

Uranium was first discovered in the Tordilla Sandstone of Karnes County in 1954. Western Karnes County was mined extensively for the U.S. Atomic Energy Commission (AEC) by a few private companies using surface mining. The first area mill was built in 1960 by the Susquehanna Company and the Western Nuclear Company. The mill was developed under a purchase agreement with the AEC for a quantity of uranium oxide to be sold at $9.90 per pound from 1960 to 1962, followed by another quantity from 1962 through 1966 to be sold at $8 per pound. This mill was one of 17 U concentrating and processing facilities in the United States at that time and had the smallest output. From 1967 to 1970 the AEC began a "buying stretchout" program, which did not include Texas, and the Susquehanna-Western mill closed temporarily. At that time AEC sales of uranium oxide were at about $6 per pound. As the demand for U by the federal government fell, sales to private companies began to increase. Exploration grew rapidly in 1968 in South Texas and throughout the United States. Surface-mining activity increased in 1969 and 1970 with three mills operating in Karnes and Live Oak Counties.

The development of in situ mining offered the prospect for production of similar quality but from deeper ore bodies. The process also posed less danger from radioactivity both during mining and afterward because the process did not entail removing the overburden, as in surface mining, and therefore did not leave behind radioactive tailings ponds. The first modern in situ U-leach mine was operated by Utah Construction and Mining Company (now Utah International, Inc.) at its Shirley Basin site in Wyoming. During 1961 to 1963, the company experimented with many techniques, particularly with regard to well-development procedures and leach solutions. From 1963 to 1969 in situ mining was the only method used by this company for U production. After 1969 the in situ leach operation was replaced by open-pit mining. The first industrial devel-

opment in Texas was in 1975 when Atlantic Richfield, U.S. Steel, and Dalco became partners in a pilot in situ U plant using the Dalco-developed process at the Clay West site near George West in Live Oak County.

The first state permit for commercial in situ mining of U in the United States was issued to Atlantic Richfield and partners for the operations at the Clay West site, effective January 1975. In October 1976 a second in situ site was permitted for the Burns Ranch site directly across the highway from the first site. At that time Texas led the nation in the production of uranium yellow cake produced by the in situ technique. In 1977 and 1978, both in situ and surface-mining operations developed and expanded, while exploration for deposits suitable for both types of operations continued to be sought. Comparisons between surface and in situ mines at this time showed that while conventional surface mines produced yellow cake for $11.83 per pound, in situ mining could produce it for $8.73. Also, lead time for the operational development of in situ mines was 2 to 3 yr, as opposed to 7 to 10 yr for surface mines. By 1980, 9 companies were mining at 25 sites by means of in situ technology, and 6 additional applications for permits had been filed. The location of the U district within the State of Texas is shown in Figure 12.1. The current distribution of in situ mines is shown in Figure 12.2, where in situ mines are found in five counties: Bee, Duval, Karnes, Live Oak, and Webb.

Demand for U slacked in 1979. The price climb had been dramatic: from $8 per pound in 1970, $10.50 in 1975, and $22 in 1976 to $43 and more for spot markets in 1978. Prices fell from $43.25 in December 1978 to $40.25 in December 1979, a 6 percent decline after the stable price high of 1978. The price continued to decline, reaching $31 in July 1980, and by September 1981 the price stood at $23.50 per pound.

Two developments accounted for much of the reduction in demand. One was the artificial demand created under the Long-Term Fixed-Commitment Enrichment Contracts, which, from their inception in 1973, caused a disparity between feed requirements that had existed years before and actual reactor needs (reflecting cancellations and deferrals). In 1979 the transition to the Adjustable Fix-Commitment Enrichment Contract was completed; it eliminated the higher, artificial demand by reducing feed requirements to more closely correspond to actual reactor needs. Another factor contributing to demand reduction was the Three Mile Island nuclear reactor accident. As a result of the accident, numerous reactor construction schedules were canceled or indefinitely deferred and start-up dates were delayed. The U.S. Nuclear Regulatory Commission ceased licensing, and the requirements for design change and retrofit remained uncertain. These developments together reduced U.S. uranium needs and delayed the dates to meet these needs. The full effects of lessened U.S. demand were not felt immediately owing to the unprecedented level of activity among non-U.S. buyers on the U.S. market; chief among them South Korea, Taiwan, Japan, Switzerland, and West Germany.

Meanwhile supply continued to grow with the momentum generated by contracts concluded during the price rise of 1974 to 1976. What was then perceived as a shortfall in supply accelerated exploration, development, and ambitious programs
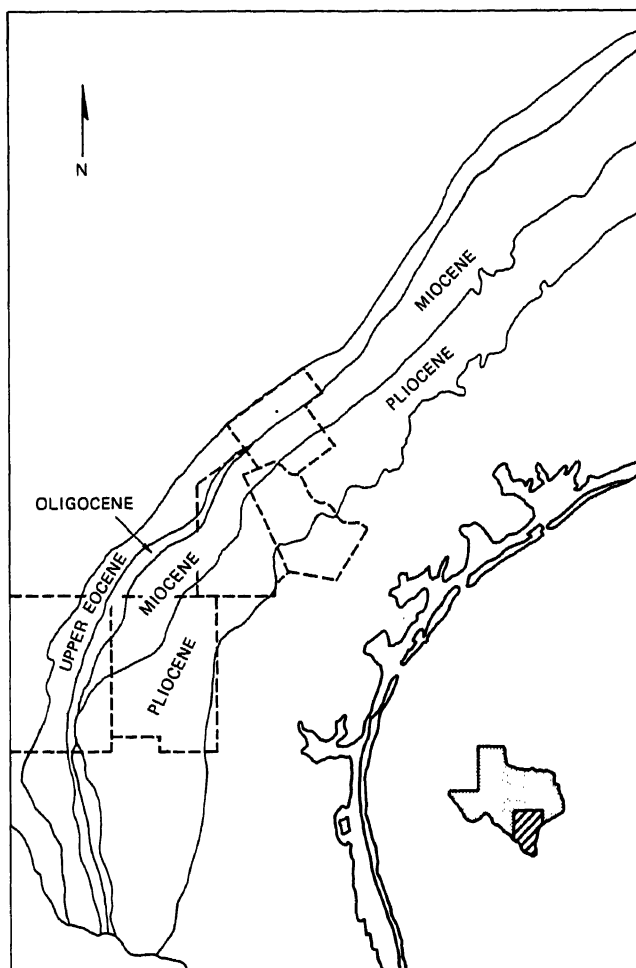
FIGURE 12.1 Geologic formations in South Texas (surface outcrops).

of expansion, not only in South Texas and the other U areas of the United States but in Africa, Canada, and Australia as well. Production during 1979, as throughout the history of the industry, exceeded consumption worldwide. Utility inventories grew steadily during the 1970s. Exploration in the United States as a whole declined 23 percent in 1979 in direct response to the drop in U prices. But activity in South Texas continued at its previous pace with in situ mining remaining the favored recovery method.

Groundwater Resources of the South Texas Mining District

The water resources of the South Texas U-mining district consist primarily of groundwater. This resource is highly variable in quantity and quality, and the impact of restoration on the resource is a question of major concern. In the South Texas region, U occurs in several different formations of the early-to mid-Tertiary clastic wedge of the coastal plain, including the Jackson Group (Eocene), Catahoula Formation (Oligocene-Miocene), Oakville Formation (Miocene), and Goliad Forma-

FIGURE 12.2 South Texas uranium mining district. The following
reference letters refer to the mine and operating company: A, Moser,
U.S. Steel Corp./N.M. Uranium, Inc.; B, O'Hern, Mobil Nufuels
Corp.; C, Bruni, Wyoming Minerals Corp.; D, Lamprecht, Wyoming
Minerals Corp.; E, Burns Ranch, U.S. Steel Corp.; F, Pawnee, In-
tercontinental Energy Corp.; G, Palangana, Chevron (Union Carbide);
H, Clay West, U.S. Steel Corp./N.M. Uranium, Inc.; I, Boots/Brown,
U.S. Steel Corp./N.M. Uranium, Inc.; J, Pawlik, U.S. Steel Corp.;
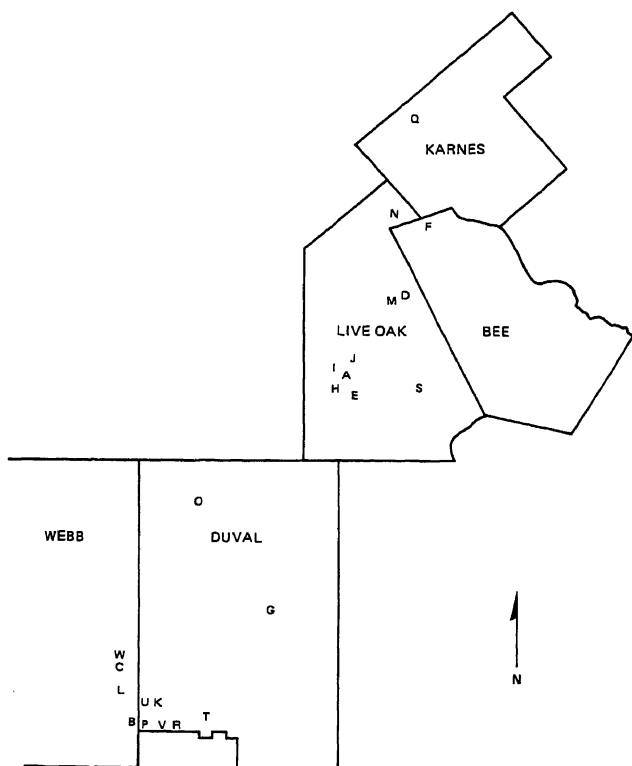K, Holiday-El Mesquite, Mobil Nufuels Corp.; L, West Cole, Tenneco
Uranium, Inc.; M, ZamZow, Intercontinental Energy Corp.; N, Nell,
Mobil Nufuels Corp.; O, Piedre Lumbre, Mobil Nufuels Corp.; P,
Longoria, Uranium Resources, Inc.; Q, Hobson, Everest Minerals
Corp.; R, McBride, Caithness Mining Corp.; S, St. Lucas, Everest
Minerals Corp.; T, Las Palmas, Everest Minerals Corp.; U, Benavides,
Uranium Resources, Inc.; V, Trevino, Conoco, Inc.; and W, Santonino
(test), Urex, Inc.

tion (Pliocene). The different formations outcrop in belts trend-
ing roughly northeastward parallel to the coast, with younger
rocks cropping out near the coast and successively older units
farther inland (Figure 12.1). The Tertiary sediments in the area
were deposited on the subsiding margin of the Gulf Coast
geosyncline, and their regional dip is gently basinward (south-
east) with some local reversal occurring along fault zones. The
sequence of rocks in the region typically thickens in the di-
rection of regional dip, until it encounters one or more belts
of contemporaneous faults. The thickness of the Tertiary sed-
iments increases greatly across these faults, coincident with a
change from fluvial to coastal plain facies (Galloway, 1977).

Precipitation on the various outcrops on the coastal plain,
and northwest of it, is the source of regional groundwater.

Nevertheless, a large part of that precipitation either runs off
at the land surface or is dissipated by evapotranspiration. Only
a small fraction of the precipitated water infiltrates the soil and
the subsoil, moving downward to the water table and becoming
part of the groundwater in storage. The general direction of
movement of the groundwater flow in the area is southeast-
ward, to the Gulf, from areas of natural recharge to areas of
natural discharge. However, this general pattern is locally in-
terrupted by concentrated pumping and local faults. Although
the topographic relief is slight, there is evidence of topographic
control of groundwater movement. The principal means of nat-
ural discharge are transpiration, evaporation, and interforma-
tional leakage, while pumped wells constitute the principal
artificial means of groundwater discharge.

Using information developed by the Texas Water Devel-
opment Board (1977), the groundwater availability in the U-
mining area of the Gulf coastal plain is estimated to be about
100×10^6 m^3/yr. This quantity exceeds the present rate of
water use of 50×10^6 m^3/yr for municipal, industrial, and
agricultural users (Charbeneau et al., 1981). Water use is not
expected to exceed 75×10^6 m^3/yr by the year 2000. Thus
under present circumstances, there is not expected to be a
water-quantity problem in this South Texas region in the near
future.

Concerning questions of restoration, the original or baseline
water quality is as important as the quantity of water. Strategies
for aquifer restoration, after the U ore has been withdrawn,
are developed with an understanding of the baseline water
quality and of prospective users of waters of varying qualities.
Dissolved chemicals are common to all subsurface waters. They
result from the leaching of materials in the soils and rocks
through which the water must pass to reach and flow in the
aquifer. Most of the groundwater used for municipal supplies
in the in situ area is fresh (0 to 1000 mg/L of dissolved solids),
though some may be slightly saline (1000 to 3000 mg/L). Since
in some cases the only water available may be slightly saline,
it is used for human consumption even though the mineral
content may be too high for certain manufacturing and indus-
trial uses. The U.S. Environmental Protection Agency (EPA)
has established maximum contaminant levels (MCL) for some
constituents in public water systems. The EPA regulations set
forth primary MCL values that are enforceable by law and
secondary values that represent reasonable qualities for drink-
ing water but are not federally enforceable. An examination of
165 wells in Duval County has shown that most of the water
sampled does not meet the MCL values in all respects and that
dissolved solids and chloride content are especially high. Again,
however, this is the best water available and is currently being
used for drinking with no obvious adverse effects (Shafer, 1974).

The major ions that normally constitute more than 90 percent
of the total dissolved solids (TDS) in groundwater are the cat-
ions sodium, calcium, and magnesium and the anions bicar-
bonate, chloride, and sulfate (Freeze and Cherry, 1979). The
exact chemical makeup is controlled by the source of water and
the path it takes through the subsurface system. For the Gulf
Coast aquifers, low-pH water near the outcrop dissolves $CaCO_3$.
As this water moves downdip, the calcium is exchanged for
sodium in clays and the sodium content increases. Bicarbonate

is the stable anion of the carbonate system at the predominant pH. As such, most waters in the Gulf Coast aquifers become sodium-bicarbonate waters downdip. As these waters continue to migrate it is common to find an increase in sulfate and particularly chloride concentrations. Baseline water-quality data for a number of South Texas in situ leach mining sites have been gathered by Humenick *et al.* (1978). These data show a TDS ranging from 700 to 2300 mg/L with highly variable cation and anion concentrations. For the cations, which are more important than the anions in terms of groundwater restoration (of ammonium), sodium is the major species accounting for 53 to 96 percent of the cations on an equivalents basis (sodium concentrations ranged from 11.1 to 30.6 meq/L). Calcium is second in importance, magnesium third. The major anions are bicarbonate and chloride.

Regulation of the In Situ Uranium Industry in Texas

In situ mining of U offers various cost and environmental advantages over surface mining but may create several types of environmental impacts if certain precautions and remedies are not followed. Among the most important of these impacts are the effects on groundwater. The state of Texas, through its policy to "conserve and develop natural resources" (stated in the Texas Water Code of 1977), has endowed various state agencies with regulatory authority over industries that develop natural resources. What sets in situ U mining apart from other kinds of in situ mining (for coal and lignite) and all surface mining, however, is that in situ U is regulated by the Texas Department of Water Resources, whereas the Texas Railroad Commission regulates all other in situ and all surface mining. This arrangement of regulatory authority over the mining industry is unique among states.

The Texas Railroad Commission (TRC) was created in 1890 by an amendment to the state constitution and charged with regulating rates and tariffs for a private, profit-making sector of the economy—the railroads. The Railroad Commission was the first regulatory agency in the state and gradually expanded its authority to cover other forms of transportation. In 1917 the Texas legislature declared pipelines to be common carriers like railroads, and thus the regulation of oil and gas transportation also came under TRC jurisdiction. When the state passed the Surface Mining and Reclamation Act in 1975 to control wastes resulting from activities associated with surface mining and the production of oil and gas, the logical agency to which the legislature turned for implementing was the TRC, which already had authority over the transportation aspects of oil and gas. Commercial in situ U mining came into production at this time. A 1977 amendment to the Surface Mining and Reclamation Act proposed to place all the regulation of in situ mining—that for coal, lignite, and U—in the hands of the TRC; as enacted in 1978, however, the amendment included coal and lignite but not U.

In situ mining of U has stood apart from oil, gas, surface mining, and in situ mining for other materials. Because of the Texas Water Quality Board's authority over wells, in situ U operators first came to this agency for permits to operate. In situ U mining has remained under the authority of the state water agency, which since 1977 has been the Texas Department of Water Resources (TDWR). The language of the state's water-quality policy was passed on from the Water Quality Act of 1967, which established the Texas Water Quality Board, to the TDWR in 1977. It reads: "to maintain the quality of water in the state consistent with the public health and the economic development of the state; . . . and to require the use of all reasonable methods to implement this policy." The implications for a mining industry regulated by the TDWR with its goal of maintaining water quality differ from the implications for all other mining industries in Texas, which are regulated by the TRC. The resulting situation has created a difference in the regulations faced by the U industry in Texas. Since the Surface Mining and Reclamation Act, land reclamation has been required for surface mining in Texas, but the mineral and energy-related industries regulated by the TRC do not have to restore groundwater affected by their operations. However, dating from the first permit issued in 1975, restoration guidelines have been included in the permit application, which the TDWR requires of the in situ U-mining companies.

The first permit, issued to Atlantic-Richfield in 1975, handled the subject of aquifer restoration in the following way. Values for the elements being checked were derived from analysis of the production area and water quality in the vicinity of production. These values were then used by the Texas Water Quality Board in light of EPA Interim Drinking Water Standards, the TWQB Hazardous Metals Board Order, and other pertinent data, to determine when adequate restoration had been accomplished. Restoration was to begin within 60 days after U production had ceased. Two conditions determine when the aquifer had been "substantially returned" to its original condition and quality: (a) if the concentrations of all hazardous metals in the baseline determination are less than or equal to those for freshwater, as determined by TWQB Board Order 70-0828-5, and all concentrations are returned to no more than 10 percent above original baseline values as determined above; (b) if the baseline concentrations of one or more heavy metals are significantly (at the discretion of the TWQB) in excess, according to Board Order 70-0828-5 for discharge to inland water, and the original water considered to have marginal potability, the prime parameter used for re-establishing the aquifer will be the total dissolved solids that must be returned to less than or equal to 10 percent above the original baseline concentration for the control grid. This permit as written in 1975 gives no schedule or deadline for when restoration should be completed. Schedules for restoration, suggested by the applicant in the permit application, do not appear until the 1979 permits.

Restoration requirements have evolved with the industry since this 1975 permit. Those for the 1980 permits are as follows: Upon completion of mining, the permittee notifies the TDWR district office and Executive Director and proceeds to re-establish groundwater quality in affected mine-area aquifers to levels consistent with values listed in the Restoration Table for the mine area. Production-zone values in this table are established by using the highest value for each parameter shown in the Baseline Water Quality Table of the permit in columns titled Mine Area Average and Production Area Average. The

overlying aquifer values are taken from the values for each parameter shown in the same table of the column titled Non-Production Zone Average. "In no instance will a Restoration Table value be established lower than the Baseline value nor higher than the Upper Limit value. Restoration values may be modified by the Commission in accordance with TDWR rules . . . by amendment to the permit if other water quality criteria warrant such action." Thus, in essence, the current restoration strategy is return to baseline.

The regulation of in situ mining by TDWR over the first 5 yr of production raises a number of critical issues both in terms of evaluating past performance and setting standards, or goals, for continued regulation in the future. The first and major issue concerns the flexibility of restoration standards. For the industry as a whole there is a question of whether the restoration strategy of return to baseline is too rigid in terms of the quantity of water and energy that will have to be used to attain this quality. From the point of view of the individual companies, the variability of restoration guidelines through time and from one site to another can give unfair advantages to some permit holders. Nevertheless, the state agency believes that restoration standards must be flexible and negotiable, because of the site specificity and evolving technology involved. Industry, too, realizes that the lack of fixed standards on which they can plan is an inevitable consequence of in situ U mining at this time.

A second regulatory issue that has been raised concerns scheduling and duration of restoration activities. As with flexible restoration standards, flexibility in scheduling and duration of restoration programs presents certain advantages to some industries. A longer duration period, for example, may be less costly for the company involved. Natural effects of water movement in the aquifer and the chemistry of heavy metals aid in restoration over time. The fact that the area water is out of use for a longer period is a disadvantage for other users and potential users in the area. However, the fact that less water is used for restoration over a longer period is a plus for other users. For most recent permits, each area is to be restored in a period of 3 to 4 yr. The principal difference among permits lies in the number of areas into which the permit is divided. The longest restoration period that has been proposed calls for restoring 16 areas, at 4 yr each, staggered over a period of 49 yr.

A third regulatory issue concerns coordination of policy for surface and in situ mining. As has been mentioned, the TDWR regulates in situ U mining in Texas, whereas surface U mining is regulated by the TRC. Restoration requirements differ for each. Regardless of the method of mining, the finished product sells on the market for the same price. Without coordination of regulatory policy between the TRC and TDWR, it is possible that companies regulated by one agency are subject to higher-cost restoration programs than are companies regulated by the other agency. Questions raised include: Should all companies mining U in Texas be subject to the same, or a similar range of, restoration costs? If it is in the interest of the state to promote one method of U mining over the other, which method should it promote, and why? Is groundwater protected to the same degree in surface and in situ mining?

A fourth regulatory issue concerns the evaluation of resto-

ration options and their impacts. A study of this issue would provide useful criteria for advocating the restoration method that offers the best long-term protection of the state's water resources. The Ford, Bacon, and Davis Utah, Inc. (1979) report addressed work in this area and could be used as a guide for making an evaluation of the various restoration options.

Restoration Activities in the South Texas Uranium-Mining District

During the early development of the industry most of the companies anticipated use of groundwater sweep with either deep-well disposal or evaporation-pond disposal to achieve restoration. It was expected that target restoration values could be achieved with production of only a few pore volumes from the sites. A review of recent restoration attempts is presented by the U.S Bureau of Mines (1981). Table 7 (page 35) of that report summarizes the results from thirteen tests, eight of them in Texas, with only one of them on a commercial site (for this site, operated by Intercontinental Energy Corporation, restoration is still ongoing). With production of from 0.5 to 15.2 pore volumes, when an ammonium lixiviant was used, the ammonium value remained far above the target value. In some cases the U concentrations approached target values; however, in most, they remained above target values. The data for the ongoing restoration at Intercontinental Energy Corporation's Pawnee property are shown in Table 12.1. Only the ammonium, molybdenum, and conductivity values remain substantially above target values after production of 2 pore volumes. After production of 15.2 pore volumes from a one-pattern field test at Wyoming Mineral Corporations Irigaray property in Wyoming, ammonium remained at 33 mg/L of N (target value less than 1 mg/L), while U (U_3O_8) was reduced to 1 mg/L (target value of 0.098 mg/L). These data show the extreme difficulty of ammonium restoration by groundwater sweep and suggest that heavy metals (particularly U) may require considerably more than a few pore volumes to return to target values.

In terms of the future development of the industry, the question of ammonium restoration is moot because operators have switched to nonammonium lixiviants. However, ammonium has been used at a number of commercial sites in South Texas, and these sites are yet to be restored to the permit's

TABLE 12.1   Data for Ongoing Restoration at Intercontinental Energy Corporation's Pawnee Site, Texas[a]

Parameter	Achieved	Target
NH_3-N	167 mg/L	0.01 mg/L
U_3O_8	2.4 mg/L	2.0 mg/L
TDS	911 mg/L	903 mg/L
Mo^{2+}	2.8 mg/L	1.0 mg/L
Cl^-	107 mg/L	250 mg/L
Ca^{2+}	80 mg/L	200 mg/L
Conductivity	1899 mho/cm	1310 mho/cm

[a]Leaching reagents, NH_3HCO_3 + H_2O_2; area involved, 75 ft × 250 ft; patterns involved, 5; restoration by groundwater sweep with reverse osmosis and spraying; pore volumes used, 2.

required values. The question of ammonium restoration has been researched at The University of Texas at Austin for a number of years. Recently, Charbeneau (1981) suggested the following relationship for the number of pore volumes (PV) required to restore ammonium to a level C_{NH_4} by groundwater sweep in an aquifer with anion concentration (C_A), cation exchange capacity (Q_V), and selectivity coefficient (K) for exchange between ammonium and sodium, which is assumed to be the predominant cation in the formation water:

$$PV = 1 + \frac{KQ_VC_A}{[C_A + (K - 1)C_{NH_4}]^2} \cdot$$

This equation is based on an analysis of mass transport (without dispersion) with the conditions of electroneutrality, filled exchange sites, and a mass-action law formulation of cation exchange. For the South Texas region, C_A varies from 11 to 31 meq/L, Q_V from 3 to 24 meq/100 g (with a porosity of 0.24 and a material density of 2.55 g/cc, these correspond to Q_V values varying from 250 to 2000 meq/L), and from laboratory studies, the value of K is about 3.5 (see Charbeneau et al., 1981). As an example, with $C_A = 18$ meq/L and $Q_V = 650$ meq/L, the number of pore volumes required to reduce ammonium to EPA drinking-water standards (10 mg/L of N; 0.71 meq/L) is 106. It should be apparent that in this example the water and energy use for ammonium restoration by groundwater sweep is excessive. The equation above, however, does suggest that water requirements can be greatly curtailed through use of recirculation with the injected fluid constituted with appropriate high ionic strength chemicals. An analysis of this type is presented by Charbeneau (1982); however, continued research is necessary.

Recently, a number of the companies have reviewed their options for groundwater restoration. The general trend is away from groundwater sweep with deep-well disposal toward recirculation with surface treatment of the waste stream before reinjection. This strategy, which involves minimal net water use, will probably become the standard for the industry if natural restoration methods are found to be insufficient. For the future of the industry, restoration research will probably focus on the fate of heavy metals. Research on leaching will continue with a search for an optimal lixiviant that is operationally effective in U recovery, will not affect the hydraulic properties of the host rock, and will not present significant restoration problems.

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V

INSTITUTIONAL ASPECTS

Selected Variables Affecting the Choice between Federal and State Regulatory Responsibility: Groundwater Quality as an Illustrative Case

13

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With the advent of the current federal administration in the United States, the debate over the appropriate roles of federal and state governments in exercising regulatory functions has become more strident. In the area of environmental policy the arguments seem particularly well drawn. Ordinarily, the presumed superior capacity of the states to comprehend their own problems and be responsive to local needs is contrasted with the federal government's presumed ability to provide momentum in pollution control policy and to resist unwarranted pressures from organized interest groups.[1] What are the most appropriate roles for federal and state governments remains an unanswered question. Earlier practical commitments to defined federal and state roles in this country's surface-water-quality and air-quality programs are being re-examined, whereas the extent of federal involvement in many aspects of groundwater regulation is still in a discussion stage.

The contention here is that the question remains unanswered, in part, because many of the variables crucial to the choice between federal and state regulatory responsibilities have not been thoroughly examined. In this chapter, at least two variables that I believe have not received sufficient attention are examined. These are the jurisdictional scope of decision-making authority and the structural distance of decision makers from information on problem conditions and on preferences of affected individuals. These variables have an important impact on the ability of decision makers to formulate efficient regulatory policies. Moreover, the scope of the jurisdiction assigned to federal decision makers often differs from that assigned to state decision makers, and federal and state decision makers are at different structural distances from the points of origin of many important types of information. The

resulting implication is that if the arguments presented here are valid, then these differences will affect regulatory efficiency and the choice between federal and state responsibilities.

Developing propositions involving jurisdictional scope and structural distance, however, is not intended to resolve the debate over the choice between federal and state responsibilities. These propositions are no more than hypotheses that can be verified only with observations from many policy areas. Also, variables other than the ones examined here certainly will have an impact on the federal-state choice. Nevertheless, these propositions can serve as part of an analytical framework within which the federal-state question can be investigated more adequately.

In the course of developing these propositions examples involving groundwater quality regulation will be used. This is done for heuristic purposes, inasmuch as characteristics of groundwater-quality problems aptly reveal dimensions of the variables to be examined. Also, the general public has become concerned about groundwater-quality problems. Discussing various aspects of these problems may facilitate their early resolution.

GROUNDWATER QUALITY AND ITS REGULATION

The quality of the nation's groundwater has for some time now been threatened by contamination from the intentional or unintentional deposition of mining, manufacturing, and agricultural wastes. The full extent of contamination is unknown, but already identified sources of contamination number in the thou-

sands [Council on Environmental Quality (CEQ), 1981; Silka and Brasier, 1980; U.S. Environmental Protection Agency (EPA), 1977]. Moreover, the pressures exerted on groundwater quality from generated wastes will likely increase as regulatory protection of surface waters and the air resource comes into full force and as the push for discovery and exploitation of new energy sources is accelerated (EPA, 1980a, p. 34). The former activity diminishes the availability of waste receptacles, whereas the latter increases the volume of waste.

Estimates pertaining to groundwater use suggest the full significance of these problems. For example, the U.S. Water Resources Council (1978, pp. 12-13) estimates that about one fourth of all freshwater used in this country is supplied by groundwater sources. This includes drinking water that services approximately one half of the U.S. population (EPA, 1977, p. 21; EPA, 1980b, p. IV-1). Most estimates also project increases in demand for groundwater in future years (EPA, 1980b, p. II-8).

Despite these estimates and despite the projected growth of contamination problems, no general commitment that authorizes the exercise of comprehensive regulatory functions in the groundwater quality area has been made to a particular government level. At the state level, groundwater quality is generally regulated only in piecemeal fashion, usually in response to some eminent hazard that has aroused public alarm. Limited regulatory activities are sometimes undertaken through loose interpretation of public-safety legislation or legislation aimed at surface-water regulation (Bartelt, 1979).

At the federal level, sporadic regulation is authorized under the sole-source aquifer provisions and underground injection control program of the Safe Drinking Water Act of 1974, under various sections of the Resources Conservation and Recovery Act of 1976, and under the Surface Mining Control and Reclamation Act of 1977. These regulations apply only to circumscribed activities (mining, hazardous-waste disposal) or to aquifers (as a sole source of a community's drinking water). Under present interpretation, however, federal laws do not authorize regulation of all activities that have a significant impact on groundwater quality. They also do not extend regulatory coverage to all usable aquifers.

Spurred on by Congressional inquiries (Interstate and Foreign Commerce Committee, 1979; Government Operations Committee, 1980; Government Affairs Committee, 1980), the EPA began an effort in 1980 to examine questions involving the responsibilities of federal and state governments in regulating groundwater. Through a series of workshops (EPA, 1980b, 1980c) and public hearings, EPA developed a policy position on regulatory responsibilities that involves an expanded federal role, though no new federal legislation is proposed (EPA, 1980d, p. VII). Through agency rule making, EPA expected to exercise guidance and approval functions in the preparation of state plans and strategies for regulatory groundwater quality. It also expected to assume primary responsibility for development of a groundwater classification system that associates protection levels with groundwater uses. Further, EPA envisioned developing and implementing national "requirements" or standards for groundwater problems on a national scale. Finally, EPA anticipated considerable financial involvement, if not lev-

erage, in the development of state strategies and state utilization of the classification system.

More recently, the present federal administration expressed a strong preference for state rather than federal responsibility for regulatory matters. Accordingly, the administration has pushed for a curtailment of the federal role envisioned in the EPA groundwater strategy. Nevertheless, I believe that consideration of an expanded federal role likely will continue — perhaps more seriously at a later date. An examination of aspects of the federal-state choice with reference to groundwater regulation is not without policy relevance.

EFFICIENCY

Before beginning such an examination, however, an investigator needs a clear idea of what criteria will be used to distinguish between inferior and superior regulatory outcomes. In other words, a concept must be defined that permits evaluation of the effects of study variables. As suggested, jurisdictional scope and structural distance often assume different values at state and federal levels. We want to predict how regulatory outcomes might be changed by these differences and also know the basis for imputing worth, positive or negative, to the changes so predicted.

A concept useful for evaluating regulatory outcomes is social efficiency. By itself, the term efficiency can take on many different meanings,[2] but here it pertains to assessments of aggregate human welfare. A regulatory outcome is socially efficient to the extent that it corresponds to what is desired by some designated population.[3] This general criterion does not, however, specify how the welfare of each individual is to be treated as a portion of aggregate welfare.

A more precise concept, commonly referred to as Paretian efficiency, suggests that a particular outcome is efficient relative to the *status quo* if it results in welfare improvement for at least some members of a designated population without, however, imposing welfare losses on other members of that population. An outcome is Pareto optimal if no other outcome (among a set of feasible alternatives) results in welfare gains for some individuals without imposing welfare losses on others.

The advantages of this evaluative criterion are several. First, it places emphasis on the actual effects of arrangements on human welfare as opposed to a variety of abstracted criteria (for example, coordination and integration), the achievement of which may or may not result in improved human welfare. Second, Paretian efficiency provides a conceptual basis for dealing with conflicts between the environmental, energy, economic, and health values commonly associated with the use of resources like groundwater. The use of this concept avoids reliance on *a priori* judgments about the relative worth of these values. Rather, it presumes that each individual can rank alternatives by weighing and trading off the perceived benefits and costs to him of the environmental, energy, economic, and health aspects of each alternative. An outcome is deemed inefficient if, on weighing its various aspects, any individual expects to suffer net costs from its occurrence. The value one individual places on an outcome does not need to be compared

with the value another individual places on the outcome to decide whether it is efficient. It follows that the distributive character of Pareto efficient outcomes cannot be, in at least one sense, adverse. Benefits accruing to some individuals are not permitted to justify the imposition of costs on others. The rich may, indeed, get richer, but not at the absolute expense of the poor.

A major disadvantage of the criterion is that in the real world a Pareto efficient alternative to the *status quo* sometimes does not exist.[4] Someone may be a loser no matter what alternative is chosen. In these situations, some other criterion must be used to evaluate alternatives.

For example, alternatives may be ordered by use of a utilitarian criterion in which the benefits and costs that each individual expects to experience from adoption of each arrangement are aggregated across all individuals of a designated population. Net benefits expected by one individual are allowed to offset, in some proportion, net costs expected by another individual. The alternative generating the highest total net benefit is regarded as the most desirable. If valid measurements can be obtained, the utilitarian criterion can be used to order virtually any set of alternatives and identify a uniquely superior alternative.

However, application of a utilitarian criterion orders alternatives only with respect to aggregate benefits and costs. The distribution of benefits and costs among individuals in the designated population does not affect the derived ordering. Inequitable distributions may sometimes be associated with outcomes that are deemed most desirable through application of the utilitarian criterion.

Because of this possibility, Paretian efficiency is employed as the favored evaluative criterion in the comparisons to follow. However, a utilitarian criterion is employed where Pareto efficient alternatives do not appear to exist or cannot be identified. In some cases, a utilitarian criterion identifies an alternative that is also Pareto optimal. With some institutional arrangements, individuals are fully compensated for any losses they incur from choice of a particular alternative. Application of a utilitarian criterion forces selection of an alternative for which aggregate benefits exceed aggregate losses by the largest amount.[5] If these excess benefits are employed to compensate initial losers so that they no longer suffer any losses, then the outcome is Pareto optimal by definition.

Hence, Paretian and utilitarian efficiency are not mutually exclusive concepts, but as evaluative criteria, they will not always point to the same alternatives. To avoid confusion in the analyses to follow, the term "efficiency" will refer specifically to Paretian efficiency (without necessarily precluding the utilitarian sense) unless otherwise stated.

Finally, we should note that practical application of these concepts can be complex or simple. Sometimes it involves the simultaneous consideration of the impacts of many variables on a multitude of other variables. More often it involves only notation that one alternative has a more desirable impact on one variable than does some other alternative. For example, we might note that federal regulation of groundwater entails fewer public expenditures than does state regulation. In this case, we assume that everyone prefers paying fewer taxes.

Second, we assume that the two alternatives have a similar impact on other variables that have public value. We might assume, for example, that federal and state regulation of groundwater would result in the same levels of groundwater contamination. Assumptions of this latter type, though common, are often tenuous. Sometimes, our only real defense of this type of assumption is that we just have no evidence, one way or the other, concerning what impact the alternatives have on other variables. This circumstance is general to many forms of systematic inquiry, however, and does not diminish the value of isolating particular relationships with the intent of clarifying their character. In the analyses to follow, I examine relationships involving jurisdictional scope, structural distance, and regulatory efficiency using groundwater-quality regulation as an illustrative case.

JURISDICTIONAL SCOPE OF DECISION-MAKING AUTHORITY

The jurisdictional scope of authority assigned to federal decision makers often differs markedly from that assigned to state decision makers. Obviously, state boundaries delineate the largest jurisdictions assigned to state-level decision makers. On the other hand, federal decision makers, especially those entrusted with important policy decisions, may have jurisdiction over the entire nation. When they do not have a national scope of jurisdiction, federal officials are likely to exercise authority over regions that encompass many states. For example, the EPA maintains 10 regional offices each of which has responsibility for regulatory efforts in regions that include from two to eight states.

These jurisdictional differences between state and federal levels imply that constituencies affecting and affected by decisions differ accordingly. Below, I argue that the efficiency of outcomes generated by regulatory institutions at these levels is likewise affected.

However, the definition of an appropriate constituency or scope of jurisdiction for making decisions about the provision of any public good (including regulatory goods) is often regarded as a normative issue. It may be argued, for example, that only those individuals or groups affected in a more than vicarious way by a groundwater policy should have a voice in the selection of that policy.[6] Indeed, a strong case can be made for this position. Individuals often hold preferences for policy outcomes that do not have any particular consequences for them. However, there is no obvious ethical reason why individuals should have influence over policies that have value for them only because they feel empathy for others or believe that the social conditions they desire for themselves should be universally pursued. Allowing these individuals to exercise decision-making influence within a particular jurisdiction results in the dilution of the influence of those who are affected by decisions in a substantive way. A sense of democracy violated seems to follow.

In principle, allowing only those individuals substantively affected by decisions to exercise influence within a defined jurisdiction does not seem to exclude consideration of the in-

terests of future generations who one day may be affected by present decisions. Because future generations cannot now exercise influence, incorporating their interests requires resolution of the operational problems of identifying what those future interests will be and who should represent those interests in the present. The magnitude of these problems may pose an obstacle to the proper representation of future generations, but the inclusion criterion expressed above does not.

Conceivably, the inclusion of only those with substantive interest may result in the exclusion of no one. In the area of groundwater regulation, for example, the regulation of a single aquifer could affect everyone because the ecology of the aquifer is changed. As part of a global ecology, changes in local ecological conditions can be expected to have ultimate global effects, however small. Thus, everyone is affected in the sense that they confront modified ecological conditions.

Global ecological interdependence may be a fact, but many particular interdependencies are likely to be trivially small. As McMillan (1976, p. 50) points out in an analogous context, if jurisdictional lines are not based on differences in the magnitude of these interdependencies, then "everyone should have a say in everything and that is not satisfactory in theory or practice."

In contrast, jurisdictional lines could be drawn in a way that accounts for differences in the importance individuals attach to the problem effects they experience or, perhaps, more practically, in a way that accounts for differences in the amount of actual problem effects (e.g., physical, economic) to which individuals are exposed. In any case, jurisdictional assignments based on each of these two criteria ought to overlap significantly. Individuals who feel strongly about a problem tend to be those who are exposed to the largest number of problem effects.[7]

McMillan (1976) examined the jurisdictional issue and found that application of an efficiency criterion complements the normative position expressed above. He demonstrated theoretically that the exclusions from a decision-making jurisdiction of some individuals who have only slight interests in an issue improved the efficiency of decisional outcomes over jurisdictional assignments in which every individual with at least a slight stake in an issue was included. The evaluative criterion applied was utilitarian efficiency with no compensation being paid to those suffering net losses from decisional outcomes. The decisional mechanism employed for choice between two alternatives is majority rule.

McMillan's results cannot yet be fully generalized to jurisdictions in which various decisional mechanisms are employed nor to situations in which many choice alternatives are possible. Even if they were, we still would be unable to project with much confidence what jurisdictional assignments would be most efficient in our groundwater example. The problem effects originating from particular groundwater aquifers are usually distinguishable from the effects originating from other aquifers. But important aquifers range in areas from less than a few square miles to dimensions transcending the borders of many states. Moreover, many of the effects of a groundwater-quality problem are physical (though not all) and limited in scope by the dimensions of the aquifer. Accordingly, jurisdictional as-

signments that encompass most individuals affected by an aquifer problem, while excluding those experiencing only slight effects,[8] will vary approximately with the dimensions of the relevant aquifers. The type of uses to which an aquifer is put, the scope of economic effects of aquifer problems, and distributional characteristics of user populations will, of course, affect the strength of this correlation.

Knowledge of these variable values is currently scarce.[9] Nevertheless, the arguments advanced here imply that a federal jurisdiction would be more efficient, other things being equal, for deciding on policies for aquifers with boundaries transcending the borders of many states.[10] For many problems, then, the dimensions of the aquifer itself define a lower bound for the scope of important problem effects. For multistate aquifers, a particular state jurisdiction is obviously too small for deciding on all regulatory policies. For aquifers with more limited dimensions, the uncertainties regarding the scope of problem effects make projections about the most efficient jurisdictional assignments speculative. Still, it seems likely that for most intrastate aquifers, important problem effects will not transcend state borders. The relationship posited here between jurisdictional scope and efficiency implies that federal regulation of these aquifers would be more efficient than state regulation.

STRUCTURAL DISTANCE

It also is hypothesized here that the structural distance of decision makers from problem conditions and from information on individual preferences affects the efficiency of institutional outcomes. With traditional federal and state arrangements, regulatory policies are decided on within representative legislative bodies or within administrative agencies authorized by these legislative bodies. The quality and quantity of information utilized by these centers in making decisions affects the efficiency of outcomes generated by them. For groundwater regulation, information about the definition, size, hydrology, quality, and uses of aquifers must be obtained as well as information on what quality levels and what uses of particular aquifers are preferred by relevant individuals.[11]

Downs (1967) and Tullock (1965) explain how information is affected by structural distance. They suggest that administrative systems with extended hierarchies deliver less accurate information to decision makers than administrative systems comprising less extended hierarchies. As information generated by the grass-roots level is passed from one hierarchical level to another, it is reduced and modified. The information is reduced so that the smaller number of individuals at the next higher hierarchical level can absorb all the information transmitted from below. The information is modified (perhaps only by discretionary reduction) to enhance the personal goals and interests of each individual who handles and interprets the information. The more levels through which the information must pass before being transmitted to decision makers, the more distorted the information is likely to become.

To make some decisions about groundwater, federal decision makers must rely on state hierarchies (or, less likely, create

parallel hierarchies) to provide them with information describing the relevant problems. In the early phases of the sole-source aquifer program, decision makers at EPA determine whether aquifers are to be categorized as sole drinking-water sources. In addition, as part of the groundwater regulatory strategy, proposed in 1980, EPA envisaged taking responsibility for devising a general groundwater classification scheme (EPA, 1980d). The details of this plan are not precisely stated but could include the analytical construction of categories defined by groundwater quality and aquifer use as well as official placement of particular aquifers into these categories. The information needed to make these decisions, especially that pertaining to existing groundwater uses and community preferences for alternative uses, is or will likely be transmitted through state as well as federal hierarchical channels. This appendage of a federal structure (characteristic of programs involving federal oversight of state programs) over which information must flow can only serve to distort further the character of the required information. Efforts to prevent distortion by creating, for example, duplicate channels of information, are usually very costly. Because state decision makers can obtain more accurate information, they should generate more efficient outcomes at least as a function of structural distance.

However, some types of information are resistant to distortion from transmission over hierarchical channels. Any information that can be codified or quantified can be transmitted without interpretation, sometimes bypassing hierarchical channels through electronic transmission. Parameters of groundwater quantity and quality are easily codified.[12] Information on these variables is likely to be as accurate when delivered to federal decision makers as it is when transmitted no further than the state level.

For other types of information, appropriate interpretation yields value. Information of a research nature often requires highly theoretic interpretation to bring comprehension to the technical nature of the problems (including institutional problems) and their solutions. Data on community preferences for alternative aquifer uses are often uncodified and largely impressionistic. Were such data to be collected in a systematic fashion, analytic interpretation of the results would still likely be needed in order that they be utilized meaningfully in the choice of aquifer use. This type of information seems particularly susceptible to summarization and distortion as it passes over hierarchical channels.

A variable that has a strong effect on the significance of information-gathering efficiency is the degree of differentiation embodied in regulatory rules. Differentiation implies that each problem source or group of sources is regulated in a different way and that the information required to assess the divergence of the source from desired behavior will also differ. With increases in differentiation, the number of decisions that have to be made in implementing a policy increases. The amount of information needed to make these decisions also increases. If a particular level of government is more efficient in collecting the necessary information, its efficiency becomes more apparent as the information collection function grows in importance.

At either the state or federal level, regulations could be promulgated that require all groundwater to be maintained at a uniform quality level.[13] Conversely, regulations might be promulgated that permit the quality level of aquifers or portions of aquifers to vary as appropriate for the present or future uses of the groundwater, the present conditions of the aquifers, their relation to drinking-water supplies, or for some other reason. A permit system that embodies such a set of regulations generates a larger number and type of decisions and more information requirements as the number of allowable quality levels increases and as the variation in contingent conditions increases.

More decisions also have to be made as the number of sources requiring permits increases. Additional information must be acquired for each source added to those already under consideration for permits. For a federal agency to be as effective as state agencies in rendering "preferred" decisions, a federal agency must, it seems, bear greater administrative costs than the administrative costs borne by the state agencies. These additional administrative costs result from the extra procedures that a federal agency must implement to avoid distortion of information as it is transmitted to decision makers.[14]

To reduce these additional administrative costs, a federal agency might opt instead to reduce the number of different decisions required. For example, the number of aquifer-use categories might be decreased. Uniform quality standards constitute the most extreme result of such a response. While reducing administrative costs, this response will create additional social costs definable in terms of costs incurred by industrial polluters. Costs incurred by industrial plants will, in part, be transferred to consumers of the industry's products. Consumers will certainly prefer an outcome where an industry's products are available at less cost. The anticipated abatement costs of an industrial plant will be less if the plant is able to locate near an aquifer that has less restrictive quality standards rather than near another otherwise identical aquifer that has more restrictive standards. The average or mean quality of the two aquifers could hypothetically be equivalent to a quality level maintained for both aquifers through application of uniform standards.[15] An industrial plant will experience additional abatement requirements with uniform standards because both aquifers will have more restrictive standards than will the less restricted of the two aquifers where differential standards are applied. A resort to uniform standards will not necessarily enable federal agencies to reduce overall regulatory costs (administrative costs plus costs borne by industry) to the regulatory cost levels of state agencies. Besides, if application of uniform standards does reduce overall costs, state agencies also can realize these savings through similar action.

The cost implications for industry of present federal regulations, state regulations, and sets of alternative future regulations could be examined in the above context. With the Underground Injection Control Program (UIC) of the 1974 Safe Drinking Water Act, for example, five classes of wells have been distinguished on the basis of their uses and their locations relative to drinking-water supplies. Each well must be placed in a class and regulated according to the requirements of that class. The reasoning expressed above suggests that expenditures made by industry to meet environmental regulations are likely to be reduced if a larger number of classes are employed

to distinguish and regulate wells. These gains must be weighed against increasing administrative costs, however, if classificatory and regulatory activities remain at the same governmental level. But if activities are moved from the federal to the state level, economies are realized in collecting information. Other things being equal, administrative costs are less at the state level. Current expectations are that most regulatory and classificatory activities of the UIC will be conducted at the state level, though continued federal oversight could serve to offset the efficiency gains in collecting information that are posited for full state responsibility.

CONCLUSIONS

In this chapter, I hypothesize that jurisdictional scope and the structural location of decision makers will affect the relative efficiency of federal and state governments in regulating groundwater quality. The arguments presented here suggest that the jurisdictional scope of state governments is more conducive to regulatory efficiency than the larger scope of the federal government when the scope of problem effects is confined to state boundaries. When problem effects substantially exceed state boundaries the suggestion is that federal regulation is more efficient, other things being equal. The scope of effects of most interstate aquifers probably exceeds state boundaries. For these aquifers, then, an efficiency advantage is attributed to federal regulation. The closer structural distance of state decision makers to problem conditions and preference information, so it is reasoned, gives them an efficiency advantage over federal decision makers when information needed for regulatory decisions is subject to distortion as it travels across hierarchical channels. Much, though certainly not all, of the information needed to make regulatory decisions about groundwater quality is of this type.

Though perhaps providing important insight, these conclusions, nevertheless, do not resolve the issue of federal versus state regulatory responsibility—even for the groundwater policy area. For this particular policy area we still lack knowledge about the precise dimensions of every groundwater aquifer. Moreover, we have not adequately determined the type and quantity of information needed to make regulatory decisions. For that matter, we do not have empirical evidence to support the hypotheses posed.

In a general sense, we also must consider other variables that affect regulatory efficiency. Differences in political pressures at federal and state levels, differences in resources, differences in legislation, and the regulatory decision rules derived therefrom are all likely to affect the relative efficiency of federal and state regulation. In some policy areas, the impact of these variables may even overwhelm the impact of jurisdictional scope and structural distance. Still, in other areas the effects of these latter variables could prove important in making a rational choice between federal and state regulatory responsibility.

NOTES

[1]National Water Commission, 1973; Okun, 1977; Congressional Research Service, 1978; CEQ, 1979. Sentiments focusing on the advantages of state-level responsibility have been expressed by various participants in the President's Task Force on Regulatory Relief.

[2]Commonly, an efficient alternative refers to the least-cost means to attainment of a preconceived objective (see Lang, 1980). This usage has only tangential relevance here.

[3]Individuals presumably account for the costs of alternative outcomes in formulating their preferences.

[4]It is also possible that more than one Pareto efficient alternative exists.

[5]We are assuming, of course, that at least one alternative exists for which aggregate benefits exceed aggregate losses.

[6]Such a list might include farmers who use groundwater for irrigation; community residents who rely on groundwater for drinking purposes; consumers of the products of an industrial or mining operation that discharges wastes into an aquifer; citizens who enjoy access to federal lands or lands of special ecological significance maintained, in part, by underlying aquifers; and taxpayers, who ultimately fund regulatory programs.

[7]For some issues, such as abortion, this logic may not hold true. Most of these issues relate to modes of personal conduct that derive from moral or religious feelings. As such, it should be easy to identify these issues and consider their jurisdictional implications.

[8]It is presumed that analyses such as McMillan's will eventually generate a specific value for the expression "slight effects."

[9]For aquifers that have special ecological significance and aquifers that may, one day, become important drinking-water sources, the relevant scope of effects will be especially difficult to ascertain.

[10]A regional or multistate arrangement might even be preferable. However, regional arrangements not subsumed under a federal umbrella have had almost no success in exercising the historically meager regulatory authority allotted to them (Ingram, 1973; Green, 1980). Here, the author focuses on the only two likely alternatives—federal and state arrangements.

[11]Keech (1979), Mosher (1979), and LeGrand (1980) provide interesting descriptions of the types of information needed for groundwater regulation and of the problems encountered in its utilization.

[12]Quantity variables include aquifer dimensions, flows, number, and location. Quality variables include salinity, acidity, biochemical oxygen demand, bacteria counts, and pollutant indices.

[13]"Nonendangerment" standards are examples of such a policy.

[14]The assumption in this case is that a significant portion of information needed for regulatory decisions is not codifiable and, hence, is susceptible to distortion.

[15]It follows that social costs resulting from pollution are conceivably, though not necessarily, similar in the two cases.

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Risk Assessment for the Prevention of Groundwater Contamination

14

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ABSTRACT

Groundwater, which is a major source of water supply in the United States, is facing severe quantity and quality problems. Once contaminated, the options available for its use are both limited and costly. The immense risks and costs to the public associated with groundwater contamination necessitate the formulation of public policy that is conducive to the prevention of this contamination.

This chapter addresses the prevention of groundwater contamination through the use of risk assessment, which embraces both the determination of costs, benefits, and levels of risks and the process of their social evaluation. Since the U.S. Environmental Protection Agency (EPA), mandated by present laws, will eventually promulgate national effluent guidelines that should be scientifically and technologically sound, economically efficient, and socially equitable, the adoption of risk assessment for this purpose seems imperative. Several recently developed risk-assessment methodologies that integrate multiobjective trade-off analysis are evaluated in terms of their effective use in the formulation of public policies leading to the prevention of groundwater contamination. Two risk-assessment methodologies—the multiobjective statistical method (MSM) and the partitioned multiobjective risk method (PMRM)—are also evaluated in terms of their specific usefulness to the EPA's ongoing effort in promulgating national effluent guidelines to limit toxic pollutants. Finally, the applicability of "economic incentives" discussed in the report by the NRC Committee on Ground-Water Resources in Relation to Coal Mining (1981) is also evaluated within the framework of risk assessment.

INTRODUCTION

Overview

Groundwater contamination is a major nationwide socioeconomic problem that has its roots in technological development. Its solution requires a scientifically sound and well-formulated public policy grounded in broad-based public participation that includes the private sector as well as the government. The lack of any one element of the above is likely to impede viable progress toward the prevention or reduction of groundwater contamination.

In considering the many different sources and causes of groundwater contamination it becomes imperative that no simple solution can address this problem adequately and compre-hensively. A comprehensive public policy that is cognizant of the multiplicity of causes and sources of groundwater contamination, that deals well with the inherent trade-offs associated with risk aversion or reduction, and that coordinates the needs of the involved multiple decision makers and constituencies can only be formulated through a lengthy process involving all concerned parties.

To prevent groundwater contamination one must be aware of the sources of contamination, understand the movement of contaminants through porous media, and understand the technical socioeconomic reasons that permit, encourage, and, indeed, make groundwater contamination the widespread phenomenon that it is today.

Central to the President's Commission on the Accident at Three Mile Island (1979) is that a group that set out to inves-

tigate a technology ended up talking about people. The Commission states: ". . . but as the evidence accumulated, it became clear that the fundamental problems are people-related problems and not equipment problems."

What clearly emerges from the Commission's report—an important theme of this chapter—is the recognition of the strong interplay that exists between man and technology and a commitment to the belief that, in the decision-making process, science and technology should be more fully integrated with social considerations.

The efficacy of the risk-assessment process for the ultimate prevention or reduction of groundwater contamination relies on the formulation of policies that are scientifically and technologically sound, economically and financially feasible, socially equitable, politically acceptable, environmentally safe, and legally compliant. People from many disciplines, constituencies, and interests must contribute to the formulation of such policies.

In this process potential risks—risks of many classifications—as well as trade-offs associated with various alternative policy options are, to the extent possible, quantified and evaluated, so that the detrimental impacts of these risks will be reduced or mitigated.

It is constructive at this point to have a more specific definition of risk. Two common definitions are presented here, one of which is adopted for this chapter. The U.S. Water Resources Council (1973) defines risk and the related concept of uncertainty as follows:

Risk situations—those in which the potential outcomes can be described by reasonably well-known probability distributions.

Uncertainty situations—those in which potential outcomes cannot be described in objectively known probability distributions.

A different definition of risk is offered by Kaplan and Garrick (1981). The notion of risk involves both uncertainty and some kind of loss or damage that might be received. They also make a distinction between risk (the possibility of loss or injury and the degree of probability of such loss) and hazard (a source of danger) and offer the following symbolic equation:

$$risk = hazard/safeguards.$$

They state that, "This equation also brings out the thought that we may make risk as small as we like by increasing the safeguards but may never, as a matter of principle, bring it to zero. Risk is never zero, but it can be small."

Because the notion of trade-offs within a framework of multiple objectives (e.g., risk, safety, cost) is central to this chapter, we will adopt the U.S. Water Resources Council's definitions of risk and uncertainty.

The risk-assessment process constitutes two major phases that partially overlap: (a) the quantitative processing and evaluation of information through well-developed procedures and methodologies, including the quantification of risk and the development of alternative policy options, and (b) the introduction of value judgment concerning what risks and their associated trade-offs are acceptable, what selections are preferred,

what policies are desirable, and what constitutes the ultimate decision (the "best compromise solution").

In evaluating alternative policy options concerning the prevention or reduction of groundwater contamination one should also inquire whether sufficient knowledge concerning the impact of contamination is available, so that the benefits from such prevention can be assessed and the additional cost incurred in the prevention of contaminated discharges can be justified. The dilemma is whether to (a) wait for additional information and thus avoid potentially unnecessary cost while risking possible negative outcomes that might even be irreversible or (b) take costly affirmative actions that might prove at a later time to have been unnecessary.

Scope and Objectives

The intended objectives of this chapter are the following:

1. Identify and articulate the risk and uncertainty aspects of groundwater contamination.
2. Identify the major sources of and causes for groundwater contamination.
3. Identify and articulate appropriate measures for the prevention of such contamination within the framework of risk assessment and trade-off analysis.
4. Formulate a hierarchical multiobjective framework that accounts for the legislative and regulatory statutory aspects at the higher level of the hierarchy and for the user/polluter aspects at the lower level. The proposed framework is intended to advance one step forward the formulation of an urgently needed, sound, effective, and credible public policy for the prevention or reduction of groundwater contamination.
5. Develop foundations for internalizing the externalities of groundwater contamination through economic incentives and disincentives along with regulatory and public education measures.
6. Explore the applicability of several risk-assessment methodologies to the proposed hierarchical multiobjective framework.

Groundwater Contamination: Sources, Reasons, and Impacts

The literature on groundwater contamination is relatively recent and dates on a significant level to the early 1950s, at which time saltwater intrusion was considered to be the dominant contaminant (Todd, 1959). The discussion in the literature has intensified only during the last decade, when the contamination of aquifers reached epidemic proportions not only in the United States but worldwide.

The "Brown Book" (Office of Science and Technology, 1966) offered the first serious call for an improved research program on groundwater contamination. In the *Second National Water Assessment*, by the U.S. Water Resources Council (1978), pollution of groundwater resources was identified as one of the critical problems facing the United States.

The Holcomb Research Institute (1977) published an important document on the utilization of numerical groundwater models for water-resource management. This report, which

addressed the modeling aspects of groundwater contamination, was later revised (Bachmat et al., 1980). During the second session of the 95th Congress, the Committee on Science and Technology (1978) conducted congressional hearings and introduced a bill concerning groundwater-quality research and development. The committee then recognized that "severe quantity and quality problems are facing ground-water systems throughout the country as ground-water resources are being contaminated and wells are being closed or depleted. There is also inadequate information about the ground-water resource, leading to increased importance of the socioeconomic impacts resulting from contamination and closing of wells."

The UNESCO International Hydrological Programme (1980) published a comprehensive report on the subject addressing the theoretical and practical aspects of groundwater contamination as well as numerous case histories from over a dozen countries. These and numerous other documents highlight the critical dimension and scope of groundwater contamination.

The sources of groundwater contaminants are numerous (U.S. Environmental Protection Agency, 1977). Among these are surface impoundments, landfills, leaks and spills, agricultural activities, land disposal of wastewaters, river infiltration, petroleum development activities, highway de-icing salt, septic tanks, saltwater intrusion, underground storage, and artificial recharge of wastewater.

The reasons for the practices leading to contamination from the above sources can be classified into five major generic categories: economics, lack of education, technology, regulation problems, and accidents.

Economics Often users/polluters avoid the additional costs required for safe discharge of hazardous wastes from their facilities. In some cases, the present legal penalties imposed by courts on the practices that may lead to contamination are less than the cost that would have accrued to the user/polluter for safe and prudent practices. Furthermore, the present socioeconomic and legal-institutional system does not induce users/polluters to internalize the external cost of pollution control.

Lack of Education A large, maybe even a dominant, portion of the population is not aware of the groundwater contamination problem or of the impacts of hazardous-waste disposal. This may be attributed to the fact that changes in groundwater quality (unlike those in surface water) are relatively slow and hidden, and their detection may only draw the attention of limited parties. Information is inadequate about groundwater resources and the socioeconomic impacts resulting from their contamination.

Technology Technology for adequate and safe disposal of certain hazardous wastes may either be unavailable or insufficiently advanced and economically impractical. This aspect is one of the most difficult to address—nuclear-waste disposal is a case in point.

Regulation Adequate regulatory measures and standards for the prevention of groundwater contamination are not available.

Often the lack of regulations is interpreted as implied permission. A later section of this chapter focuses on this.

Accidents Although accidents that may cause contamination cannot be completely prevented, measures can be taken to reduce their frequency and scope. In many cases contaminants in high concentrations are spilled within a short time. Analysis of accidents should provide a basis for a better understanding of their causes and ultimately should provide for more viable control mechanisms.

Table 14.1 suggests a framework that relates the sources and reasons for groundwater contamination, thus providing a more systematic mechanism for the risk-assessment process and policy formulation. The impacts associated with Table 14.1 can be classified, for the purpose of risk assessment, into four generic categories: (1) human health hazards (known and unknown), (2) environmental degradation, (3) economic hardship, and (4) social dislocation. The quantification of these impacts constitutes a critical basis for the risk-assessment process.

Groundwater-Quality Modeling

A brief introduction to groundwater-quality modeling is presented in Anderson (1981). Three primary types of models are in use today: advection, advection-dispersion, and geochemical models. In advection models, contaminants are carried along by water flow. Advection-dispersion includes the effect of microscopic dispersion (which is negligible in comparison with macroscopic dispersion). Geochemical models normally simulate the evolution of groundwater quality considering reactions involving calcium, magnesium, and sulfate.

The two-dimensional advection-dispersion model for mass transport developed by Konikow and Bredehoeft (1978) is one of the most useful models available today. The aquifer is permitted to be isotropic or anisotropic, as well as heterogeneous. This model was successfully incorporated in a risk analysis study of groundwater contamination (Kaunas, 1982; Kaunas and Haimes, 1983).

Fractures in rocks can greatly speed the transport of contaminants underground. Tang et al. (1981) developed an analytical solution for pollutant transport along a thin discrete fracture located in a saturated porous rock. Numerical results for various conditions closely match those generated by the fracture simulation model of Grisak and Pickens (1980).

Groundwater-management models generally combine a transport simulation model with an optimization technique to find optimal well locations, pumping rates, or other objectives. An aquifer behaves linearly in the steady-state case, so that an efficient linear program can be formulated with the discretized governing equations as constraints (Willis, 1979). The same method can be applied to the nonlinear case, but this gives a large constraint matrix. Gorelick et al. (1979) used a recursive scheme to increase the efficiency of this method.

Moosburner and Wood (1980) developed a land-use management model and applied it to Jackson Township of the New Jersey Pine Barrens. Charbeneau (1981) developed a model for

TABLE 14.1 Possible Framework Relating Sources and Reasons for Groundwater Contamination, Which Can Be Site or Regional Specific

Sources of Contamination	Reasons for Contamination				
	Economics	Education	Technology	Regulations	Accidents
River infiltration					
Runoff					
Natural recharge					
Herbicides, insecticides, fertilizers					
Irrigation return water					
Land spreading of sludges					
Well development					
Septic tanks					
Municipal and industrial sewer systems					
Landfills					
Waste disposal					
Storage of minerals					
Recharge of wastewater					
Shallow wells					
Well injections into saline aquifers					
Underground storage (waste, heat)					
Surface and subsurface mining					
Acid mine drainage					
Disposal of feedlot waste					
Gas and oil field activities					
Pipelines					
Highway de-icing salt					
Saltwater intrusion					

contaminant transport in groundwater with adsorption and ion-exchange reactions using the method of characteristics. Gorelick and Remson (1982) and Gorelick (1982) developed a groundwater-quality management model that uses a linear programming formulation. Other management models have used specific discretized versions of the governing equations as a set of constraints in linear and nonlinear programs.

THE MULTIOBJECTIVE FRAMEWORK

Determining the acceptability of risk is undoubtedly one of the most complex and difficult decision-making problems facing public officials. Lowrance (1976) posed this all-encompassing problem in one sentence: "Who should decide on acceptability of what risks for whom, and in what terms, and why?" Starr (1969) distinguished between voluntary and involuntary risk as a basis for determining the acceptability of risk. Slovic *et al.* (1979) focused on the perception of risk and its dominant influence on the acceptability of risk. Rowe (1977) provided some methodological approaches for risk assessment. Schwing and Albers (1980), in the book they edited, set as their objective a thorough discussion of social risk assessment and how safe is safe·enough. Fischhoff *et al.* (1980) stated: "Acceptable-risk decisions are an essential step in the management of technological hazards. In many situations, they constitute the weak (or missing) link in the management process. The absence of an adequate decision-making methodology often produces in-decision, inconsistency, and dissatisfaction. The result is neither good for hazard management nor good for society."

Common and central to the above-cited writings is the fundamental premise that determining the acceptability of risk (within the risk-assessment process) is grounded in determining and evaluating trade-offs among the various objectives and/or attributes (Haimes, 1981). These multiple objectives are often noncommensurable, in conflict, and in competition. A specialized field—multiple criteria decision making (MCDM)—has emerged during the last decade, focusing on decision making with multiple objectives. Although the concept of Pareto optimality dates back to the nineteenth century, the intensive development and use of quantitative approaches for optimizing multiple objectives is a relatively recent phenomenon. Heuristically, a Pareto-optimal solution for a multiobjective optimization problem, also known as an efficient and noninferior solution, is any solution for which one objective function can be improved only at the expense of degrading another. In addition, the notion of best is interpreted here as the preferred solution selected by a decision maker(s) from within a Pareto-optimal set of solutions. The following is a more formal definition of this concept for the problem: minimize [$f_1(x)$, $f_2(x)$, ... $f_n(x)$]. A decision x^* is said to be a noninferior solution to the above-posed problem if and only if there does not exist another $\bar{x}$ so that $f_j(x) \leq f_j(x^*)$, $j = 1, 2, \ldots n$, with strict inequality holding for at least one j. Germane to MCDM and to risk assessment is the dominant role of the decision maker(s) in selecting preferred policy options.

Example Problem

An oversimplified problem concerning groundwater contamination with trihalomethanes (THMs) is presented as an example of the overlap between risk assessment and multiobjective optimization. The contamination is caused by landfills used as dump sites for hazardous chemical wastes under the jurisdiction of and controlled by City Z. Given that the U.S. Environmental Protection Agency (EPA) has not as yet promulgated regulations in compliance with the Resource Conservation and Recovery Act (RCRA)—a fact that is causing a significant delay in issuing permits—City Z, to a large extent, must make its own risk assessment. About 50 percent of the city's water supply is pumped from the aquifer contaminated by THMs.

The simplified version of this problem can be posed as follows. Let x denote the vector of decision variables (options) available to City Z. The city has a set of feasible disposal options, X. Thus, $x \in X$ (the decision vector x belongs to the feasible set X). Associated with each policy x are a cost function, $f_1(x)$, and a risk function, $f_2(x)$. The most common unit for measuring cost is the dollar. The risk, on the other hand, may be measured in a number of ways, the simplest being the concentration of THMs in parts per billion (ppb). This surrogate indicator can in turn be used to determine a more direct measure of risk to health involving perhaps the probability of death and sickness.

The risk-assessment/multiobjective optimization problem can be posed as

$$\underset{x \in X}{\text{minimize}} \ [f_1(x), f_2(x)] \qquad (14.1)$$

or find the "best" policy x that would simultaneously minimize the cost and the risk.

A noninferior solution of this multiobjective problem is one in which any reduction of the cost of pollution control can be achieved only at the expense of increasing the risk of contamination. The surrogate-worth trade-off (SWT)—a method for analyzing and optimizing multiple, noncommensurable, and conflicting objectives—constitutes the backbone of the risk analysis in the multiobjective framework presented here.

The trade-off values between the ith and jth objective functions $f_i(x)$ and $f_j(x)$, respectively, are denoted by λ_{ij}. These λ_{ij}'s are generated by the SWT method and have been shown to satisfy the following relationships:

$$\lambda_{ij} = -\frac{\partial f_i(x)}{\partial f_j(x)}, \ i \neq j; i, j = 1, 2, \ldots n, \qquad (14.2)$$

where $\lambda_{ij} > 0$ is a sufficient condition for j noninferior solutions. Note that it is sufficient to generate only one row vector of the trade-off matrix, e.g., $\lambda_{12}, \lambda_{13}, \ldots \lambda_{1n}$, and to derive all other trade-offs from this vector. Figure 14.1 depicts the plotting of cost versus risk in the functional space. In comparing the three policies, x_A, x_B, and x_C, chosen to lie on the Pareto-optimal frontier, it is evident that policy x_A results in much lower levels of THMs concentration than do either x_B or x_C [$f_2(x_A) < f_2(x_B)$ $< f_2(x_C)$]; however, it also results in much higher costs [$f_1(x_A)$ $> f_1(x_B) > f_1(x_C)$]. Thus the reduction of an additional amount of THMs (which is equivalent to reduction of risk to public health) translates into an increase in cost. Models, such as the mass-transport model of Konikow and Bredehoeft (1978), can relate a concentration response in a well to a spill input. Such models are most valuable for the quantification of the functions $f_j(x)$ (Kaunas, 1982).

The most critical phase (in MCDM and risk assessment) is, of course, determining the "best" solution, namely, determining exactly what level of risk is acceptable. There are several available methodologies that are capable of generating as many Pareto-optimal solutions as deemed necessary, and they provide systematic procedures for the decision maker(s) to reach that best solution. The SWT method is such a methodology, and it generates in addition all the respective trade-offs associated with the Pareto-optimal solutions (see Haimes and Hall, 1974). These trade-offs are essential for determining the acceptability of risk by the decision maker(s). The slope of the

FIGURE 14.1 Pareto-optimal solutions and trade-offs.
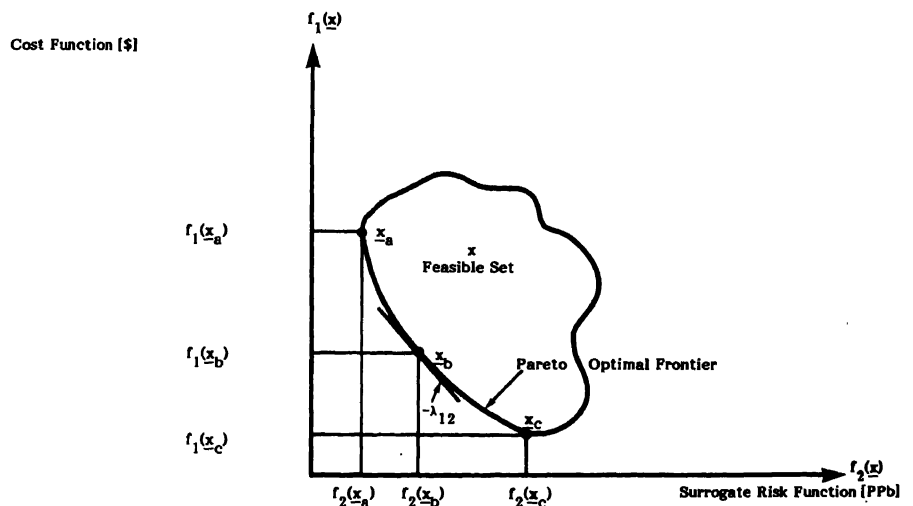
tangent to the Pareto-optimal frontier at x_B is the trade-off associated with $f_2(x_B)$ and $f_2(x_B)$, as is depicted in Figure 14.1. Note that the units of λ_{12} are the ratio of the units of $f_1(x)$, and $f_2(x)$, namely \$/ppb. The SWT method assists the decision maker(s), by means of the surrogate-worth function, to arrive at the best-compromise solution, also known as the preferred solution. Because the scope of this chapter must be limited, the interested reader should explore the literature for further elaboration on the SWT method and its extensions and on MCDM in general (see, for example, Chankong and Haimes, 1983).

INTERNALIZING THE EXTERNALITIES OF POLLUTION

The exponential growth of the chemical industry manifested in the development and manufacture of thousands of new products annually has inundated the government bureaucracy. Indeed, the EPA and the National Cancer Institute are capable of testing only a small portion of new products with respect to their environmental and/or health hazards. This is because of the exceedingly high cost of testing and the time involved.

A fundamental question remains unanswered: is it the responsibility of the manufacturer-producer to ensure the public safety and the integrity of the environment from the adverse effects of new products; or is it the role of government, as the representative and protector of the public, to do so; or is it both? The issue is particularly critical and urgent with respect to the disposal of residual wastes.

The national experience accumulated over the last decade in the control and abatement of surface-water pollution and air pollution should not be overlooked when considering the pollution of groundwater resources. Public Law 92-500, which was enacted in 1972 and called for a "zero discharge," ignored, in principle, the economic realities of the marketplace. Following the recommendations made by the National Commission on Water Quality in 1976, Congress enacted the Clean Water Act of 1977 (Public Law 95-217). The Commission stated (National Commission on Water Quality, 1976):

Wise use of total national resources would support the imposition of only those levels of control or treatment that actually produce the intended results. Additional investment with only marginal identifiable benefits or improvements could operate to the detriment of competing demands of other worthwhile national programs, such as energy conservation and air pollution control.

Therefore, measures that are aimed at preventing groundwater contamination should be based not only on sound scientific, technological, and environmental considerations but also on sober socioeconomic realities. In this respect, a viable system of economic incentives and disincentives should be an integral part of and constitute firm foundations upon which regulations for contaminant/pollutant discharge standards are formulated. A recent report issued by the National Research Council stresses these points (NRC Committee on Ground-Water Resources in Relation to Coal Mining, 1981). The report stated, "The problem of institutional design and implementa-

tion is the final step necessary to ensure that ground-water conflicts, present and future, are resolved in an environmentally responsible, economically efficient, and socially equitable manner."

On the economic incentives, the report stated, "*Economic incentives*, either rewards or penalties, may be used to 'internalize' externalities (both spatial and temporal) and thus to induce voluntary compliance with social goals." Economic incentives may be created in two ways: (1) through the establishment of liability rules that define the rights and duties of private individuals or organizations and (2) by involving government more directly either as an imposer of taxes, charges, or fines to discourage inappropriate behavior or as a source of tax credits, loan guarantees, or other forms of positive incentives to encourage appropriate behavior.

It is worth noting that a system of effluent charges for surface water has been implemented successfully in Germany, where the Ruhr and Emscher Genossenschaften have administered a program of environmental control for almost a century (Federal Water Pollution Control Administration, 1970, pp. 143-160).

Thus, in order to prevent groundwater contamination it is worth investigating the efficacy of effluent charges and a system of economic incentives and disincentives—concepts well suited to the management of surface-water pollution (see Kneese and Bower, 1968; Hass, 1970; Kneese *et al.*, 1970; Haimes, 1971, 1977; and Maddock and Haimes, 1975). The process of risk assessment facilitates juxtaposing the risk of an event and the cost associated with the prevention of that risk. Hence a system of economic incentives and disincentives, when adequately and appropriately backed up by legislation, can serve as a potent measure for the prevention or reduction of such a risk. The socially equitable level of these economic measures can be determined (as will be discussed in more detail in subsequent sections) via trade-off analysis as part of the multiobjective optimization procedure and the risk-assessment process.

QUANTITATIVE ANALYSES

Introduction

For pedagogical purposes, it is constructive to digress, dividing the risk-assessment process into three major, though overlapping, elements.

1. Information management: including data collection, retrieval, and processing through active public participation.
2. Model quantification and analysis: including the quantification of risk and other objectives, the generation of Pareto-optimal policies with their associated trade-offs, and the conduct of impact and sensitivity analysis.
3. Decision making: the interaction between analysts and decision makers and the exercise of subjective value judgment for the selection of preferred policies—policies for which the risks are deemed to be acceptable to the decision makers within the overall trade-off analysis.

Although these elements are easily identified, the state of the art in risk assessment is still in its infancy concerning the

many uncertainties associated with each element, in particular, the lack of knowledge in quantifying the causal relationship between the sources and reasons of groundwater contamination and the contamination's impacts. These uncertainties further complicate the third element—the decision making and exercising of subjective value judgment. These impediments, nevertheless, should not, in any way, prevent the use of risk assessment for policy decision, particularly for public-policy decisions such as those concerning the prevention of groundwater contamination.

The information-management element is discussed elsewhere in this volume (Chapter 13) and thus will not be addressed here. This section will be devoted to generic model quantification and analysis, keeping rigorous mathematical developments to a minimum, though these will be supplemented with proper references for readers whose interests and orientation are more mathematical.

Generic Model Formulation

This section addresses the generic quantification of the causal input-output relationships between sources of contamination (What can happen?) and the impacts and damages of such contamination (If it does happen, what are the consequences?) in a framework that couples these causalities with the probabilities of occurrence (How likely is it that that will happen?) (see Kaplan and Garrick, 1981).

In the formulation of models, five groups of variables need to be defined.

1. *Decision variables* (x). These are measures controllable by the decision makers, such as legislation, promulgation of regulations, zoning, public education, and economic incentives and disincentives. The symbol x denotes a vector of such decision variables, $x = (x_1, x_2, \ldots x_n)$.

2. *Input variables* (u). These are materials discharged and/or entering the groundwater system. These input variables are not necessarily controllable by the public decision makers but rather are controllable by the individual parties involved in the contamination of aquifers. Input variables include, for example, the discharge of THMs, synthetic organic contaminants (SOCs), trichloroethylene (TCE), and saltwater intrusion due to pumping. For a more parsimonious notation and without loss of generality, the system's inputs and outputs are lumped into u. For example, water pumpage and artificial recharge can both be conveniently considered as part of the vector u in the context of modeling groundwater contamination. The symbol u denotes a vector of such input variables, $u = (u_1, u_2, \ldots u_m)$.

3. *Exogenous variables* (α). These are variables related to external factors, albeit affecting the system either directly or indirectly. Theoretically, these exogenous variables could encompass the entire universe excluding x and u. For practical purposes, however, exogenous variables such as the physical characteristics of an aquifer; water demand for industrial, urban, and agricultural development; technology assessment; and economic market forces may be considered. The symbol α denotes a vector of such exogenous variables, $\alpha = (\alpha_1, \alpha_2, \ldots \alpha_p)$.

4. *Random variables* (v). A probability-distribution function (Pdf) may or may not be known for each random variable. For example, knowledge of probability distributions for random events such as precipitation and streamflow (and thus for natural recharge of aquifers) can be assumed. On the other hand, Pdfs for random events such as accidental spills may not be known, and uncertainty analysis rather than risk analysis should be conducted. The symbol v denotes a vector of such random variables, $v = (v_1, v_2, \ldots v_q)$.

5. *State variables* (s). These are variables that may represent the quantity and quality level (state) of the groundwater system at any time. Examples of such state variables include the water-table level, concentration of salinity, and THMs or biological contamination. The symbol s denotes a vector of such state variables, $s = (s_1, s_2, \ldots s_k)$.

The next step constitutes defining all objective functions (including risk functions) and constraints. Here, a critical distinction must be made between the objectives of the polluter and those of the public and its representatives. The risks and costs of dumping hazardous chemical wastes, for example, are certainly different for the polluter than for the user of the contaminated groundwater. To maintain realism in generic model development, here, a simple two-level hierarchy is introduced (Haimes, 1977).

The aquifer system can be decomposed into N subsystems, each of which may be affected by a different party. In a degenerate and extreme case, all N subsystems can collapse into one system—the entire aquifer. The first (lower) level of the hierarchy consists of the various subsystems/users. The second (higher) level of the hierarchy consists of an overall coordinator with powers to promulgate regulations for discharge standards and impose economic incentives and disincentives. A similar two-level hierarchical model for the planning and management of groundwater is discussed in detail by Maddock and Haimes (1975).

From the above definitions, it is clear that the five variables (vectors) are not all independent of each other. For example, the state of the groundwater system (s) depends on the quantity of contaminants (u) disposed of, what measures (x) are taken to prevent contamination, the frequency at which such contamination occurs (v), and the physical characteristics (α) of the aquifer. Thus, $s = s(x, u, v, \alpha)$.

Therefore, the various objectives and constraints of the subsystems/users can be written as functions of the state vector (s), whereby dependence on x, u, v, and α is implicit.

Let $f_j(s)$ represent the jth objective function of the subsystem/users, $j = 1, 2, \ldots J$. For example, let

$f_1(s) =$ cost in dollars of contamination prevention,

$f_2(s) =$ "risk" of contamination with THMs,

$f_3(s) =$ "risk" of contamination with saltwater intrusion.

The risk functions can be represented in numerous ways. For example, their representation can be in terms of probability and consequence, expected value, utility function, or other functions.

In subsequent discussion in this chapter more than one representation will be used. Often no knowledge of the probability-

distribution function for a specific random variable may be available, in which situation one of the methodologies for uncertainty analysis, such as the uncertainty/sensitivity index method (USIM) (Haimes and Hall, 1977), may be used.

Similarly, all the system's constraints (e.g., physical, economic, institutional) can be defined as $g_i(s) \leq 0$, $i = 1, 2, \ldots$ I. The set of all feasible solutions/policies (X) that satisfy all the constraints can be defined as $X = [x|g_i(s) \leq 0, i = 1, 2, \ldots I]$.

The overall mathematical formulation of the groundwater contamination-prevention problem seeks to minimize all objective functions (in a multiobjective sense) via selection of the best feasible decision variables/measures, x. Mathematically this can be represented by

$$\underset{x \in X}{\text{minimize}} \ \{f_1(s), f_2(s), \ldots f_j(s)\},$$

where s = s(x, u, ν, α).

Before discussing various methodologies for the quantification of risks associated with groundwater contamination, the institutional framework must be further discussed in a form compatible with the mathematical model. For this purpose, the hierarchical multiobjective framework introduced in the next section is intended to act as a bridge among the quantitative aspects of (1) risk assessment, (2) the determination of the acceptability of risk through decision making and the exercise of value judgment, and (3) the desired institutional and other socioeconomic measures that would provide a basis for implementation of contamination-prevention policies.

A Hierarchical Multiobjective Framework

Of the numerous problems and issues related to water-resources planning and management, those associated with groundwater are undoubtedly the least studied, yet the most complex. In particular, the planning and management of groundwater resources is plagued by legal and institutional impediments (Haimes, 1980). In the eastern and midwestern portions of the United States, for example, groundwater law is judge-made law, deriving from the English common-law rule of absolute ownership, whereby each landowner was allowed to pump water from wells on overlying land without restriction (Corker, 1971). The central question that should be raised is: What is the efficacy of risk assessment in the prevention of groundwater contamination in light of present institutional and legal realities? The principal answer is grounded in the Resource Conservation and Recovery Act (RCRA) of 1976 (Public Law 94-580) and the Clean Water Act (Public Law 95-217) and, to a lesser degree, in the Toxic Substances Control Act (Public Law 94-469). The fourth objective of the RCRA is "regulating the treatment, storage, transportation, and disposal of hazardous wastes which have adverse effects on health and the environment." The EPA, charged by Congress to promulgate regulations and standards for toxic discharges, is currently working on issuing new permits for the control of toxic pollutants. The EPA is concentrating on 129 priority toxic pollutants selected on the basis of the frequency of their occurrence in water, their chemical stability and structure, the amount of the chemical produced, the availability of the chemical produced, and the availability of applicable chemical standards and measurements (Silva, 1981). This National Pollutant Discharge Elimination System (NPDES) permit program, which was established by Congress when it passed the 1972 Federal Water Pollution Control Act Amendments (Public Law 92-500), constitutes the basis for the following proposed hierarchical multiobjective framework.

In principle, a region (system) having boundaries that can be determined on the basis of political-geographical or hydrological considerations may be subdivided into N subregions (subsystems). In any region all potential contaminant discharges (which may contaminate groundwater, for example) are controlled by the EPA's NPDES permit program. The policy decisions at the higher level of the hierarchy are controlled by the EPA. The users/polluters (whether industry, farms, or municipalities) constitute the various lower-level subsystems. Clearly, the parties at both the lower and higher levels aspire to multiple noncommensurable goals and objectives that are likely to be in conflict and in competition. Furthermore, the elements of risk manifested in these objectives and the acceptability of these risks are perceived, evaluated, and traded off differently by the lower-level and higher-level parties. However, since the parties at each level have considerable degrees of freedom in selecting the most appropriate measures (within the permitted set of feasible options) that lead toward achieving their objectives, a coordination mechanism for the entire system is most desirable.

Tractable mathematical coordination schemas of hierarchical multiobjective models have recently been developed (see Haimes and Tarvainen, 1981, and Tarvainen and Haimes, 1982). In these models, each subsystem is allowed to optimize (in a multiobjective Pareto-optimal sense) its own set of objectives subject to specified constraints and limitations, and the preferred solutions generated by each subsystem are coordinated within the objectives of the higher-level subsystem (the EPA in this case). The latter generates its own modified preferred policy, and, through the use of economic incentives and disincentives (in the form of Lagrange multipliers, trade-offs, and shadow prices) along with other measures (regulatory standards and educational programs), the higher level induces the lower-level subsystem to perform acceptably.

Because the scope and level of the mathematical presentation must obviously be limited, there will be no further discussion here of the coordination scheme. However, the implications of such a scheme should not be overlooked. Through risk assessment, the EPA can evaluate the trade-offs associated with promulgating specific pollution-discharge standards in terms of the following questions (Kaplan and Garrick, 1981):

1. What can happen (i.e., what can go wrong)?
2. How likely is it that that will happen?
3. If it does happen, what are the consequences?

In addition, the EPA can incorporate additional questions concerning socioeconomic impacts, the cost to industry, and other political-geographical considerations.

The user/polluter can in turn conduct his own risk assessment, posing the same three basic questions, albeit from an

entirely different (and more parochial) perspective. The consequences brought up in the third question may include the cost of potential lawsuits in addition to the more obvious civic responsibility of the user/polluter to the protection of public health and the integrity of the environment.

RISK-ASSESSMENT METHODOLOGIES

The purpose of this section is to consider the efficacy of two recently developed risk-assessment methodologies (that integrate multiobjective trade-off analysis) and to evaluate them in terms of their effective use in the formulation of public policies leading to the prevention of groundwater contamination. These are (1) the multiobjective statistical method (MSM) and (2) the partitioned multiobjective risk method (PMRM). Two other multiobjective risk-assessment methods—the uncertainty/sensitivity index method (USIM) and the risk/dispersion index method (RDIM) described, respectively, by Haimes and Hall (1977) and Rarig and Haimes (1983)—while applicable here, will not be discussed.

The Multiobjective Statistical Method

The multiobjective statistical method (MSM) was developed for the U.S. Army Corps of Engineers to account for the risk of floodings in the design of interior drainage systems (Haimes et al., 1980). The method is an integration of a multiobjective scheme [the surrogate-worth trade-off (SWT) method] and a statistical procedure to assess the probability of a risk event and its consequences.

Problem Definition

To better understand the MSM, consider the risk of groundwater contamination due to a polluted river that traverses the aquifer, where recharge is induced by stream infiltration. The following variables can be defined:

(1) Random variables, v:

v_T^m, storm event that is associated with a storm hyetograph characterized by a sequence of given rainfall intensities and durations, $m \in [1, 2, \ldots M]$;

v_2^i, river stage, $i \in [1, 2, \ldots I]$;

v_3^l, contaminant (THMs) event, $l \in [1, 2, \ldots L]$.

(2) Input variables, u:

u_1, discharge of polluted effluents into the river by industry 1;

u_2, discharge of polluted effluents into the river by industry 2;

u_3, pumpage rate.

(3) Exogenous variables, α:

α_1, water withdrawals (demand);

α_2, nominal aquifer transmissivity coefficient;

α_3, nominal aquifer storage coefficient.

(4) Decision variables, x:

x_1, effluent charges;

x_2, standards promulgated by EPA for effluent discharges;

x_3, construction of advanced wastewater treatment plants.

(5) State variables, s:

s_1, groundwater table;

s_k, concentration of contaminant k in the groundwater.

Other random, input, decision, exogenous, and state variables can be introduced as appropriate.

The following sample of objectives and constraints can be defined:

$f_1(s)$, cost of contamination prevention;

$f_2(s)$, expected value of THM concentration;

$f_3(s)$, expected value of number of cancer patients due to carcinogenic groundwater contaminants.

The quantification of these objective (risk) functions in terms of expected values, which account for the probability distribution functions of the random variables v, is the essence of the MSM. The construction of $f_j(\cdot)$'s is discussed in the next section. The constraints are

$g_1(s)$, total budget available;

$g_2(s)$, effluent standard limitations;

$g_3(s)$, upper limit on pumpage rate.

Thus, the set of all feasible solutions, X, is defined as

$$X = \{x | g_i(s) \leq 0, \, i = 1, 2, 3\}.$$

The overall mathematical formulation of the risk-assessment problem is given by

$$\underset{x \in X}{\text{minimize}} \, [f_1(s), f_2(s), f_3(s)].$$

Construction of Risk Functions

Often the most convenient way to construct risk (as well as other objective) functions is in terms of the state variables rather than the decision variables. For example, a risk function associated with health hazards can be more easily constructed in terms of the level of contaminant concentrations (state vector s) than in terms of the measures taken to prevent such a contamination (decision vector x). On the other hand, in the multiobjective optimization and trade-off analysis part of risk assessment, it is much more convenient to have these functions expressed explicitly in terms of the decision vector x rather than the state vector s. The MSM resolves this dilemma by constructing these risk and other functions in terms of the state variables, and, through simulation and regression analysis, regenerates these functions in terms of the decision variables (specific steps will be discussed subsequently).

The other problem that needs to be resolved is incorporating the effects of the random variables into the model. This is accomplished by dividing the range of each random variable into a sequence of disjoint intervals. The events defined by this partitioning are mutually exclusive and collectively exhaustive. This partitioning is indicated by the sets $\{1, 2, \ldots M\}$, $\{1, 2, \ldots I\}$, and $\{1, 2, \ldots L\}$ for the random variables v_T^m, v_2^i, and v_3^l, respectively.

The major steps of the MSM are the following:

1. Determine the feasible set of decisions/measures, **X**, for the prevention of groundwater contamination.

2. Determine relevant historical records associated with the random variables, $\boldsymbol{\nu}$, and from these data determine the probability-distribution functions.

3. Construct the risk and other objective functions in terms of contamination levels as $\bar{f}_j(s)$, $j = 1, 2, 3$.

4. Construct the state variable vector (groundwater table and concentration of contaminants) in terms of the input vector, **u**, decision vector, **x**, and random-variables vector, $\boldsymbol{\nu}$. In general **u** is dependent on **x** [i.e., **u(x)**].

5. Specify the levels of rainfall events, M, river stage intervals, I, and levels of contaminant events, L.

6. Generate, for example, via simulation, $M \times I \times L$ values of the state vector s for each set of decisions, $\mathbf{x}^k$, $k = 1, 2, \ldots K$. Also, generate all joint and/or conditional probabilities associated with the random variables, $\boldsymbol{\nu}$.

7. For predetermined values of the exogenous variables, $\boldsymbol{\alpha}$, substitute for each set of decisions $\mathbf{x}^k$, $k = 1, \ldots K$, the values of the state vector, s, in the risk and other objective functions. The result is

$$\bar{f}_j[s(\mathbf{x}^k, \nu_1^m, \nu_2^i, \nu_3^l)], \ j = 1, 2, 3; \ m = 1, 2, \ldots M;$$
$$i = 1, 2, \ldots I; \ l = 1, 2, \ldots L;$$
$$k = 1, 2, \ldots K.$$

8. Based on the multiplication theorem of probability, generate for each $\mathbf{x}^k$ the expected value of $\bar{f}_j(\cdot)$, denoted by $f_j(\mathbf{x}^k)$, using the joint and/or conditional probabilities (as appropriate).

9. Given the set of ordered pairs,

$$[\mathbf{x}^k, f_j(\mathbf{x}^k)], \ k = 1, 2, \ldots K; j = 1, 2, 3,$$

use a regression-analysis technique (such as least-squares) to determine the functional relationship

$$f_j(\cdot): \mathbf{x} \rightarrow f_j(\mathbf{x}); j = 1, 2, 3.$$

At the completion of this stage, the expected values of all risk and other objective functions are expressed in terms of the decision vector **x**.

10. Use the surrogate-worth trade-off method to (a) generate Pareto-optimal solutions, (b) generate corresponding trade-off values, and (c) determine the decision maker's preferred solution and levels of acceptability of risk.

The use of expected value, while a sound approximation of the frequency-versus-damage risk distribution in many circumstances, falters when extreme events are considered. High-damage/low-frequency events and low-damage/high-frequency events appear mathematically equivalent in the expected value context. The partitioned multiobjective risk method, through a partitioning scheme, circumvents the drawback of the expected-value approach by constructing risk functions that can be evaluated in a multiobjective framework (Asbeck and Haimes, 1983).

The Partitioned Multiobjective Risk Method

Two seemingly unrelated problems—the multiobjective optimization problem and the quantification of probabilistic damages—have been over the years addressed in a similar, albeit somehow deficient, way. Until the early 1970s the weighting approach was the dominant solution for multiobjective (vector) optimization problems, converting multiple noncommensurable objectives, through a set of normalized weights, into a scalar objective (utility) function. These weights have been purportedly held to represent the decision makers' preferences among the various objectives. These preferences, moreover, are implicitly assumed to be constants and, thus, independent of the relative levels of each objective function. Methodologies developed in the early 1970s, such as the SWT method, avoid these precommensuration impediments, and through the use of Pareto-optimal solutions (policy options) and their associated trade-offs, the decision makers are assisted in determining a preferred/compromise solution.

A similar situation has prevailed in the quantification of probabilistic damages, or risk functions, through the use of the expected-value concept. In the classical expected-value approach, extreme events with low probability of occurrence are given the same proportional weight/importance (in the multiobjective commensurate process) regardless of their potential catastrophic and irreversible impact. Yet it is a commonly acknowledged fact that the outcome of a catastrophic accident that may cause 10,000 deaths with a low frequency of 10^{-5} is neither perceived nor accepted to be in the same category of more common accidents that occur with a much higher frequency of, say, 10^{-1} but that may cause the death of one person each time. It is argued here that the mathematical artifice— weighting coefficients in the form of probabilities—used in the expected-value approach is basically the same as that used in the conversion of a multiobjective optimization problem into a scalar single-objective problem. Thus, in this sense, the expected-value concept is as deficient and has the same flaws as the multiobjective weighting method.

A common way of describing the risk associated with an event has been through its cumulative probability distribution function. The random variable may be, for example, the spillage of a contaminant. A conventional means of dealing with this randomness has been to employ mathematical expectation or expected value to the random variable. Much information about extreme events is concealed in the expectation process. The PMRM seeks to reduce this information loss by modifying the expectation procedure (Asbeck and Haimes, 1983). In essence, the probability distribution function is divided into several segments, e.g., three segments, according to the exceedence probability of an event. A modified expectation (a conditional expectation) is taken over each of these segments, resulting in functional relationships between spillage and groundwater contamination. The central motivation in developing the PMRM is to provide a description of risk that is fuller than that of expected value. The particular aim here is to separate, for scrutiny by the decision makers, low-probability/high-damage events from high-probability/low-damage events. Another way of viewing this motivation is in terms of optimistic and pessimistic attitudes. One may relate assigning high importance to low-probability/high-damage events as a pessimistic attitude or assign less importance to these events as an optimistic attitude (Haimes, 1982).

To explain the PMRM, the concept of triplets introduced by Kaplan and Garrick (1981) will be used as a vehicle for developing risk distributions for each choice of the state vector, and it directly arrives at a means of constructing the multiobjective risk functions.

A triplet begins with an outcome scenario, sc, that describes a specific occurrence. Related to that scenario are a statistical frequency of the occurrence, ϕ, and a resulting damage, d. Thus, a triplet—$\langle sc, \phi, d \rangle$—has been created that describes the scenario. Notice that the three pertinent questions in a risk analysis have been answered: (sc) answers what can happen, (ϕ) answers how likely it is to happen, and (d) answers what detrimental consequences would ensue. Given any particular course of action, a variety of scenarios could be envisaged, each with an associated frequency and damage. For the example problem, each course of action is completely described by the components of the state vector s. By exhaustively listing all scenarios, frequencies, and damages for a specific s, the risk (R) associated with s will be enumerated. Mathematically,

$$R(s) = [sc_j(s), \phi_j(s), d_j(s)], j = 1, \ldots J,$$

where J scenarios have been listed. To bring reason to this list, reorder the subscripts, j, so that the damages obey

$$d_1(s) < d_2(s) < \ldots < d_J(s).$$

Then a cumulative frequency may be defined as

$$\phi_j(s) = \sum_{k=j}^{J} \phi_k(s), j = 1, \ldots J.$$

The cumulative frequency, $\phi_j(s)$, describes the frequency of exceeding a particular damage level. The risk associated with the course of action s is now described by the set of damage and cumulative frequency pairs. Mathematically,

$$R(s) = [\phi_j(s), d_j(s)].$$

This enumeration process may be repeated for each specific s.

Here, the digression begins to bear fruit. Each curve $R(s)$ may now be approximated by a smooth curve similar to Figure 14.2, via some curve-fitting technique such as the least-squares used in the MSM.
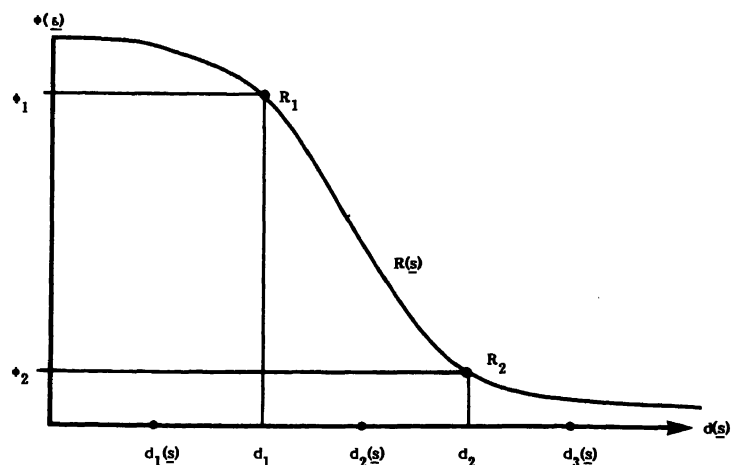
The PMRM extends this concept as follows. The risk distribution is separated into any number of distinct ranges k ($k = 1, \ldots K$). Figure 14.2 shows high-, intermediate-, and low-frequency ranges. The frequency axis of the risk distributions for each specific state s may be segmented identically by choosing the same partitioning values Φ_1 and Φ_2 for each. Associated with the frequency-axis segments will be segments on the risk curve (defined by R_1 and R_2) and on the damage axis (defined by d_1 and d_2). These R_1, R_2, d_1, and d_2 are not arbitrary: they are dictated by the choice of Φ_1 and Φ_2 as seen in Figure 14.2. A weighted average of the damage associated with each frequency-axis segment, k, may be computed and designated by $\hat{d}_k(s)$ for every $k = 1, \ldots K$.

Looking across all values for the state vector s reveals a set of point pairs $[s, \hat{d}_k(s)]$ for each frequency segment $k = 1, \ldots K$. In a manner similar to Figure 14.3, a smooth curve $f_k(s)$, $k = 1, \ldots K$ may be fitted through each of these point sets to reveal a set of damage functions corresponding to each of the frequency-axis segments. The example depicted in Figures 14.2 and 14.3 has three damage functions that describe high-, intermediate-, and low-frequency levels. These may be expressed in a multiobjective format as $\{f_1(s), f_2(s), f_3(s)\}$.

In the example developed in the section on the MSM, multiobjective risk descriptions could be developed for the second and third objectives. The damage ordinate would take on the appropriate dimensions: the THM concentration and the number of cancer patients due to carcinogenic groundwater contaminants, respectively.

EPILOGUE

The underlying premise of this chapter is that risk assessment can provide the foundations upon which a successful program for the prevention of groundwater contamination can be built. This risk-assessment process is grounded on the use of systems modeling and improved decision-making processes based on quantitative as well as qualitative/subjective analysis.

The findings of a recent study conducted by the Office of Technology Assessment (OTA) (1981) on the efficacy of mod-
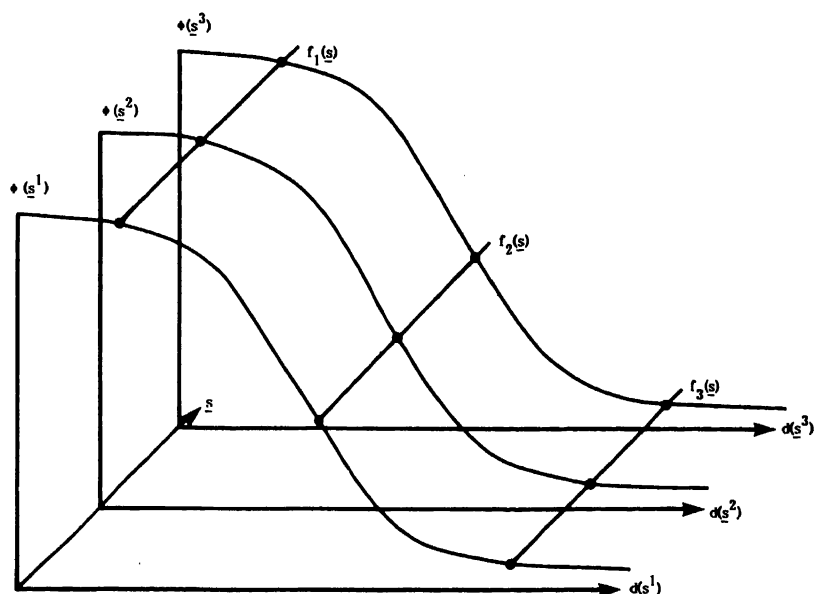
FIGURE 14.2   Risk distribution in terms of frequency versus damage for a particular choice of the state vector s.

FIGURE 14.3 Weighted average of damages for each frequency axis segment viewed across choices of the state vector s.

eling in water-resources management, planning, and policy are particularly pertinent here. The OTA study states:

Mathematical models have significantly expanded the nation's ability to understand and manage its water resources. They are currently used to investigate virtually every type of water resource problem; for small- and large-scale studies and projects; and at all levels of decisionmaking. In some cases, they have increased the accuracy of estimates of future events to a level far beyond "best judgment" decisions. In other areas, they have made possible analyses that cannot be performed empirically or without computer assistance. Further, they have made it feasible to quantitatively compare the likely effects of different resource decisions.

The above OTA findings, which are congruent with this chapter's premise, should be studied with respect to their implications on research and development needs. On the subject of improving federal problem-solving capabilities, the OTA report states:

Many of the analytic responsibilities mandated by federal and state water resources legislation cannot adequately be carried out without models. However, the analytic tools needed to fulfill many legislative requirements and decisionmaker information needs are currently unavailable. The majority of federal agencies have no overall strategy for developing, using, disseminating, and maintaining these tools.

And finally,

Unless clear direction and priority-setting mechanisms are provided by Congress and the Executive Office of the President, the best analytic tools will not be available throughout the Federal Government, and many needed models will not be built.

From the above it is evident that although risk assessment and the decision-making process associated with it can lead to the prevention or reduction of groundwater contamination, a concerted research and development effort in this area is imperative.

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